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INDUSTRY TECHNOLOGY ASSESSMENT OF GRAPHITE-POLYIMIDE COMPOSITE MATERIALS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Langley Research Center
Hampton, Virginia 23665

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INDUSTRY TECHNOLOGY ASSESSMENT OF GRAPHITE-POLYIMIDE COMPOSITE MATERIALS

Prepared Under Contract NAS 1-12436
McDonnell Douglas Astronautics Company
Huntington Beach, California 92647

for the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Langley Research Center
Hampton, Virginia 23665

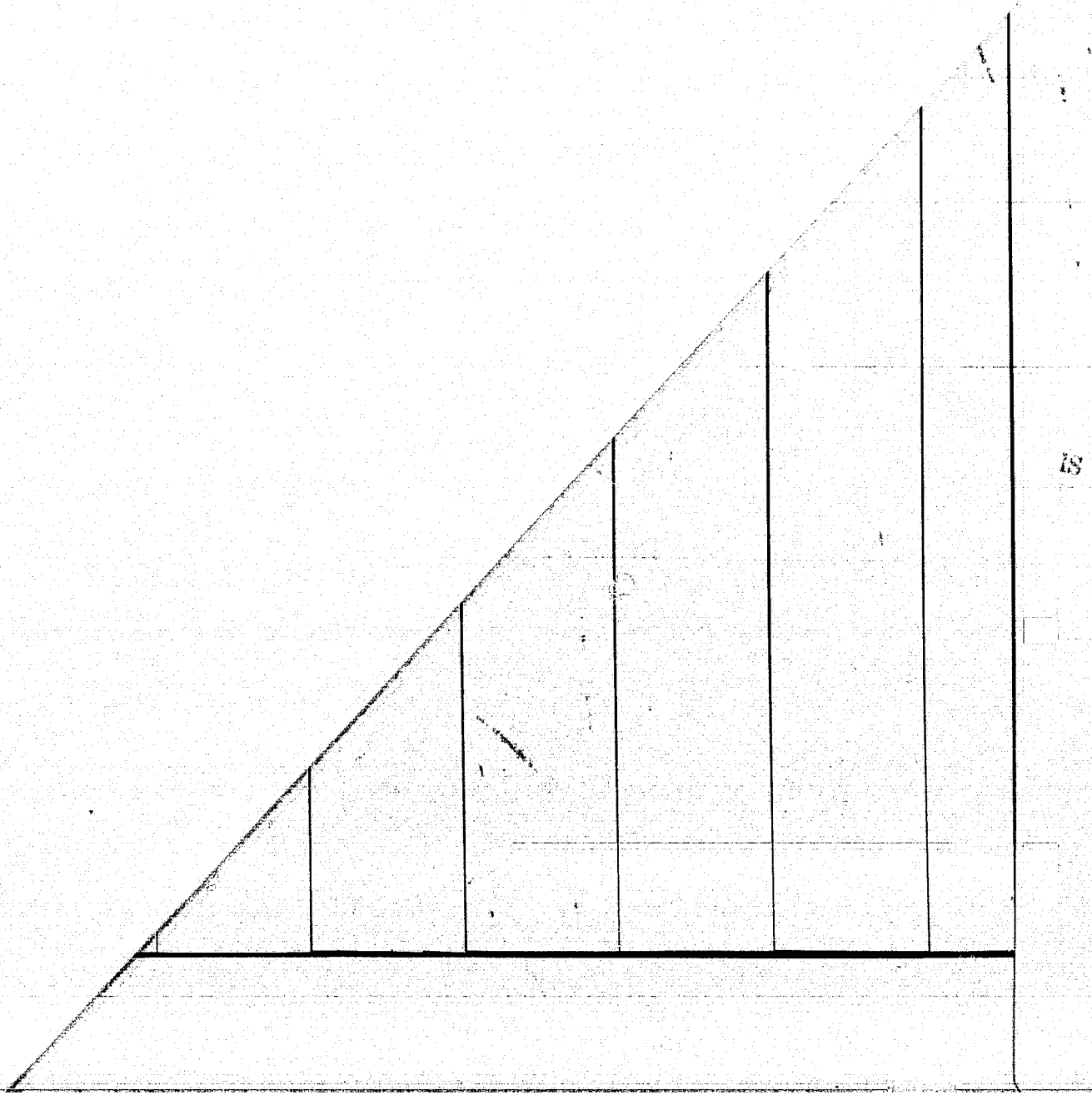
PREFACE

This report was compiled by the McDonnell Douglas Astronautics Company (MDAC) as Task 517 under Contract No. NAS1-12436 with the National Aeronautics and Space Administration (NASA), Langley Research Center, Hampton, Virginia. The report summarizes an industry assessment of graphite-polyimide composite material technology. A three-day conference was held 17-19 March 1975. The task was administered and the conference convened under the direction of Mr. R. H. Christensen, Manager of the System Design Studies (Structures) Program, MDAC. At NASA-Langley Research Center, the work was monitored by Mr. J. R. Hall, head of the Systems Design Studies Program, with Dr. John G. Davis, Jr. acting as Technical Advisor and Task Manager. Mr. Ira Petker, of Composites Horizons, was selected as the chairman for the three-day conference at the Williamsburg Conference Center, Williamsburg, Virginia.

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INTRODUCTION 1



Section 1
INTRODUCTION

NASA-Langley Research Center is planning to initiate a research and development program to demonstrate in five years the capability of graphite-polyimide composites for structural applications at 600°F to meet requirements for advanced space transportation systems, payloads, and future aircraft. The research and development program will include the design, manufacture, and ground tests of a demonstration structural component such as a major portion of the body flap, elevon, vertical tail, or payload bay door of the Space Shuttle Orbiter. The program will include a three-year developmental effort on processes for manufacturing structural components with currently available polyimide matrix and adhesive resins, characterization of material properties after exposure to various environments, and determination of design allowables for structural elements and joining techniques.

In the preliminary planning for this program, the Materials Division elected to obtain an independent assessment of the current state of the art and the future prospects for graphite polyimide composite material technology. Accordingly, the Composites Section of the Materials Division prepared a questionnaire covering the key issues and asked the McDonnell Douglas Program Office on 6 February 1975 to distribute it to a select group of specialists in composite materials. On 14 February 1975, the McDonnell Douglas Program Office distributed the questionnaire to the selected panel members with detailed instructions for their response and their subsequent participation in a three-day minisymposium/working group meeting at the Williamsburg Conference Center in Williamsburg, Virginia. During the three-day session on 17-19 March, representatives of those companies under subcontract to NASA Contract No. NAS1-12436 made formal presentations of 20 to 40 minutes each and entered into discussions of major issues on the present and future use, availability, processing, manufacturing, and testing of

graphite polyimide composite materials. A summary of the responses to the key-issues questionnaire is given in Section 4; the unedited responses are given in full in Appendix A. Section 2, prepared by the elected chairman of the meeting, Mr. Ira Petker, summarizes the presentations and discussions that were given during the conference; the unedited presentations, including illustrations, are given in Appendix B.

CHAIRMAN'S SUMMARY OF THE MEETING 2

Section 2

CHAIRMAN'S SUMMARY OF THE MEETING
By Ira Petker

PART A. TECHNICAL HIGHLIGHTS

During a two and one-half-day period, all polyimide resins known to the 10 industry conferees were reviewed in detail. The primary concern was with those resins which offered potential for moderate pressure processing. The following conclusions and recommendations were formulated.

Material Development

1. There is little to be anticipated in new polyimide resins that will radically change the state of the art.
2. The true time/temperature capability of current materials should be established when they are subjected to thermal-cycling, combined loads, etc.
3. Resin development in the CASTS Program should be restricted to modification via reformulation of current materials to optimize their performance and processability and define their usefulness and limitations.
4. The foregoing should be accomplished in 18 to 24 months.

Hardware

1. Dual objectives should be considered:
   a. Low risk utilizing the more processable resins limited to 500°F (achievable in three years).
   b. High risk with other resins for 600°F.
2. Design and materials should be treated together as co-existing variables.
3. Manufacturing innovation and scale-up techniques should be encouraged and treated from the outset as manufacturing, not laboratory, problems.

4. There was great concern that the structures developed be successful. Whether structure that can be used at a temperature of 500°F, or 600°F, or both, is developed, substantial benefit will be contributed to the technology of composites if either structure is successful.

Three types of resins, either proven or with a high probability of good performance at 600°F, were discussed. These were the condensation polymers, typified by Skybond resins, addition types such as PMR resins, and thermoplastics of the NR-type. Of these materials, the most experience reported was for Skybond resins. Shear strength values of about 8000 psi after 500 hours at 600°F were reported by several of the attendees. However, achieving this level of performance consistently and especially outside of a laboratory environment has been a problem. This was attributed to the moisture sensitivity of the polyamic acids as well as variability in the prepolymer solutions.

Very similar performance was reported by several attendees for a class of addition polymides best known for a commercial product designated as P13N. This type of material has found limited application to aerospace structure due to the high temperatures, short reaction times, and high melt viscosity attendant on their polymerization. A more recent form of this type of material, referred to as PMR resins, was reported to overcome some of the earlier problems and have potential for autoclave molding.

The NR-type resins were reported to have extremely good thermo-oxidative stability as well as good structural capability at 600°F, although there is some conflict in the latter data. This material has not been characterized sufficiently within industry to clearly assess its structural capability. It is, however, the third important, and a potentially practical, candidate for 600°F performance.

The bis-maleimide resins received considerable attention during the discussion, with a number of attendees reporting on their good fabrication characteristics. The useful temperature for these materials is limited to about

500°F. However, they may prove to be a useful stepping-stone toward the 600°F goal since the nature of the structural problems to be overcome at 500°F or 600°F should be similar.

Aside from the FM-34 adhesive, which is based on a condensation polyimide, there does not appear to be any commercial adhesive for use at temperatures between 500° and 600°F. Even for FM-34, problems in processing and variability were reported; in many respects, these were similar to the condensation polyimide laminating resins.

In few other respects were the polyimides reported to have unique problems which would prevent or limit their use. If the processing problems of the polyimides discussed above can be solved, all of the attendees agreed that the major goals of NASA's CASTS Program can be achieved.

PART B. CHRONOLOGICAL REVIEW

The NASA Graphite/Polyimide Conference was, for me, a notable experience. I came to the meeting secure in my understanding of polyimides as resins, more so as compositing resins, and of what we can expect in building and in the performance of polyimide composites. However, I had never been a chairman for quite this type of meeting, being in the middle of polymer scientists and engineering specialists representing powerful companies, knowing that some of my positions are still controversial, and with a very structured and yet a very loose program. The physical surroundings at Williamsburg were pleasant.

The meeting was scheduled for two and one-half days with 10 industry panel members; guests representing interested government agencies were in the audience.

I had thought originally that NASA would profit most from the meeting if it were to be very informal, with the audience participating actively in the discussion. Clearly, it turned out, NASA did not want this and audience participation was limited. NASA's primary purpose was to obtain the

assessment of the invited industry guests with minimal impact from the audience. In retrospect, and especially in light of the good comments I have had about the meeting, I now recognize that the overall organization of it was well conceived.

The First Day

Most of the first day was given to viewgraph presentations by the panel members. Even though the day of viewgraph presentations was very formal, I missed a sense of direction. The most controversial occurrence of the first day was Bill Scheck's report of early data which suggested that degradation due to the combination of heat, oxygen, and cyclic loads upon composite structural performance may be greater than the degradation due to any one of these alone. The suggestion was that for long-term application, the maximum operating temperature may have to be reduced 50° to 100°F from the short-term values, which is a severe penalty not only for polyimides but for epoxies as well. A minor controversial point might have been my suggestion that NR-150-type resin might not be as capable structurally at temperatures of 600°F and above as other polyimides.

There was considerable enthusiasm on the part of the polyimide users for bis-maleimide-type resins due to their simplified processability even though there was little enthusiasm for their use above 500°F. Steve Hirsch, as a polymer scientist and resin manufacturer, supported this point of view, if not as to chemistry, at least as to attainability. Milan Maximovich presented a case for thermoplastic continuous filament composites, suggesting significant simplification of processing by the application of metalworking techniques to this type of material. NR-150-type resin is reported to be a thermoplastic.

In addition to the foregoing, Bob Politi gave a broad presentation on adhesives covering basic materials, processing, and future materials. Condensation polymers are the most capable current adhesives, but these are tricky and require special venting techniques.

Hirsch presented a nicely conceived table of what industry would like in an optimum polyimide, but he did not think it all achievable in a 600°F polymer.

Hugh Gibbs reported a variety of data for NR-150 materials and stressed their toughness. He considered these the ultimate materials in thermo-oxidative stability. Sheck provided data for a variety of resins as well as some interesting applications and recommendations. Ron Kollmansberger reported his experience from various programs and concluded that variability and therefore reproducibility has been a nagging problem. He suggested a program plan for the future. Al Markhart gave a broad summary of data for Skybond resins; much of it pertained to glass reinforcement. Stan Yoshino described the many applications he has had with polyimides, exploiting their low flammability. He also showed some data from studies where composites are being considered for the Space Shuttle. Bill Winters gave a very enthusiastic report of his experience with the PMR-type resins, mostly as compression molding materials.

Prior to the formal meeting, NASA provided each panel member with an identical set of questions (topics) covering extensive ground between future, higher-performance materials and the safety, costs, and very current practical status of polyimide/graphite composites. Each panel member had responded to these topics in writing. However, each member did not respond to all of the questions, nor were their responses explicitly related to each question or subquestion*.

As I was attempting to synthesize the feeling of the panel, taking into account not only what was written but also the sense of the responses, I found much unanimity in the replies. Upon reading the summary of the responses prepared by the McDonnell Douglas Program Office and included in this volume, I found it to agree well with my recollection and my notes taken during the first day. It is concise and accurate. Thus, regarding availability, health hazards, specifications, and nondestructive testing, there did not appear to be any unique problem presented by polyimides. There was difficulty in quantitatively assessing relative performance between various resins, and little information given on the cost premium involved in fabricating hardware with polyimide, especially large-area structures. But then, there has been only minimal experience with such applications.

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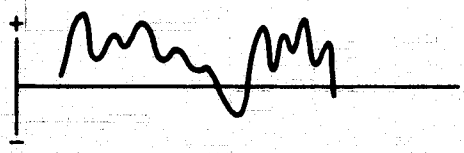
*The NASA questionnaire is given in another part of this report as well as the responses of each panel member.

After the presentations, most of the remainder of the first day was devoted to an informal discussion, lasting about one and one-half hours, over the organization of the remainder of the conference. We were helped by Eldon Mathauser of NASA/Langley who gave us a cogent description of NASA's planning to date. The program filled out the technology base and culminated in high-temperature hardware over a five-year period. Rather than having in mind at this time a specific application, the goal was to extend the useful structural life of graphite composites to the operating temperature of 600°F. Applications might range between a Space Shuttle and a workhorse airplane. With this as a focus, Kollmansberger set up a table of temperature/time/application regimes for various types of vehicles.

A specific objective of the meeting became the determination of where the state of the art of polyimide resins stood in relation to this spectrum of performance and how much closer the technology might be able to move during the next few years toward providing materials to satisfy the broad potential requirements. There was also a desire to hear more details of Scheck's study of polyimide thermal capability. Also, there was a desire to explore adhesives further. With these things in mind, the meeting adjourned for the first day.

The Second Day

The second day began with a more detailed description of Bill Scheck's current test program. It involves the application of random loads as depicted below



at various elevated temperatures. Epoxies are being tested from 200° to 350°F for up to 5000 hours and polyimides up to 550°F for 2000 hours in the presence of normal and reduced oxygen pressure. The results to date primarily involve epoxies, and the indications are that a maximum operating temperature of 250° to 275°F might be required rather than the 350° to 375°F currently accepted. Thus, by analogy, a polyimide considered

acceptable to 550°F based on traditional types of testing might only be good to 450°F. One of Scheck's conclusions is that the severity of the degradation is due to oxidative instability since there is far less rapid degradation at reduced oxygen pressure.

The remainder of the day was devoted to an in-depth discussion of each of the four major types of polyimide resins. These were the bis-maleimide resins, Skybond resins (representative of early condensation results), A-type/NASA resins, and thermoplastic resins. We used the NASA topics as a guide and a matrix of time/temperature parameters based on Kollmansberger's table to assess performance. For the latter, interlaminar strength was used for reference purposes. I suggested a value of about 16 ksi at room temperature as being attainable for all of the polyimides that were to be discussed. This is also a level of strength at which the best graphite/epoxy composites perform and it was generally agreed that at room temperature, both graphite/epoxy and polyimide composites have comparable structural capability if the composites are of equal quality. It was also noted that at this level of shear strength, a value of about 250 ksi would be anticipated for flexural strength.

All interlaminar shear strength values reported in tables 1 to 4 were determined from or are predicted for specimens which are exposed to the thermal environment only and do not include the effect of load combined with exposure.

Table 1 resulted from the discussion of bis-maleimide resins or, more generally, the straightforward addition-reaction polyimides. The various temperatures and times at these temperatures between 10 and 50 000 hours are listed in table 1 as well as time in years. The column heading "Now" means current status and "Two Years" signifies short-term potential. At each point in time, shear strength levels of 12 to 4 ksi are shown. Within the boxes of tables 1 to 4, the letter "A" signifies that the actual values are achievable based on current data; the letter "P" denotes that the values are probably achievable, and the blank boxes indicate that the levels are unlikely.

Table 1

TECHNOLOGY FOR GRAPHITE/POLYIMIDE PRIMARY STRUCTURES
BIS-MALEIMIDE RESINS

Test and Exposure Conditions		Shear Strength (ksi)					
		Now			Two Years		
Temperature (°F)	Time (hr)	12	8	4	12	8	4
450	50 000			P		P	P
	10 000		P	A		A	A
	1000	A	A	A	A	A	A
500	50 000						P
	10 000			P		P	A
	1000		A	A		A	A
550	50 000						
	10 000						
	1000			P(1)			P(2)
600	10 000						
	1000						
	500						
	100						
	10						
650	10						
700	100						

(1) 10 hours, not 1000

(2) 100 hours, not 1000

A	Achievable based on current data
P	Probably achievable
	Unlikely

Table 2

TECHNOLOGY FOR GRAPHITE/POLYIMIDE PRIMARY STRUCTURES
A-TYPE/NASA RESINS

Test and Exposure Conditions		Shear Strength (ksi)					
		Now			Two Years		
Temperature (°F)	Time (hr)	12	8	4	12	8	4
450	50 000	P	P	A	P	P	A
	10 000	P	A	A	P	A	A
	1000	A	A	A	A	A	A
500	50 000		P	P	P	P	P
	10 000	P	A	A	A	A	A
	1000	A	A	A	A	A	A
550	50 000		P	P	P	P	P
	10 000	P	P	A	A	A	A
	1000	P	A	A	A	A	A
600	10 000		P	P		P	P
	1000	P	P	A	P	P	A
	500	P	A	A	P	A	A
	100	P	A	A	P	A	A
	10	P	A	A	P	A	A
650	10			A(1)		P	A
700	100						A

(1) 50 hours, not 10

A	Achievable based on current data
B	Probably achievable
	Unlikely

Table 3

TECHNOLOGY FOR GRAPHITE/POLYIMIDE PRIMARY STRUCTURES
SKYBOND RESINS

Test and Exposure Conditions		Shear Strength (ksi)					
		Now			Two Years		
Temperature (°F)	Time (hr)	12	8	4	12	8	4
450	50 000			P		P	P
	10 000		P	A		P	A
	1000	A	A	A	A	A	A
500	50 000			P			P
	10 000		P	A		P	A
	1000	A(1)	A	A	A	A	A
550	50 000			P			P
	10 000		P	A		P	A
	1000		A	A		A	A
600	10 000			P		P	P
	1000			A		P	A
	500		A	A		A	A
	100		A	A		A	A
	10		A	A		A	A
650	10		A	A		A	A
700	100			A			A

(1) 2000 hours data

A	Achievable based on current data
P	Probably achievable
	Unlikely

Table 4

TECHNOLOGY FOR GRAPHITE/POLYIMIDE PRIMARY STRUCTURES
THERMOPLASTIC RESINS

Test and Exposure Conditions		Shear Strength (ksi)					
		Now			Two Years		
Temperature (°F)	Time (hr)	12	8	4	12	8	4
450	50 000		A	A	P	A	A
	10 000	A	A	A	A	A	A
	1000	A	A	A	A	A	A
500	50 000		A	A	P	A	A
	10 000	A	A	A	A	A	A
	1000	A	A	A	A	A	A
550	50 000			P		P	P
	10 000		P	A	P	P	A
	1000	A(1)	A	A	A	A	A
600	10 000			P(2)		P	P
	1000		A	A		A	A
	500		A	A		A	A
	100		A	A		A	A
	10		A	A		A	A
650	10			A		P	A
700	100			A			A

(1) 2000 hours, not 1000

(2) 4000 hours, not 10 000

A	Achievable based on current data
P	Probably achievable
	Unlikely

Throughout these discussions, the idea was to be optimistic about each material. Especially when it came to predicting the future, to defining the potential for each material that might result from further development, new formulations, or new resins, the intent was to build from optimism rather than pessimism.

For bis-maleimide, current performance was assessed to be 12 ksi at 450°F after 1000 hours (see table 1). It was also felt that there is a reasonable probability to anticipate 8 ksi at 450°F after 10 000 hours, 4 ksi at 500°F after 10 000 hours, and 4 ksi at 550°F after 10 hours. Within two years, 8 ksi at 450°F and 4 ksi at 500°F after 10 000 hours will probably be demonstrated. Also within two years, it was felt that 4 ksi at 450°F after 50 000 hours might be achievable as well as 4 ksi at 550°F after 100 hours. It is worth noting again that these levels have already been observed or are the best that the attendee felt would be achieved.

In the ensuing discussion of the bis-maleimides, it was noted that all have good chemical resistance, should resist ultraviolet radiation well, and perform with little outgassing under high vacuum. The health hazards in using these materials are minimal with good housekeeping practices. Preimpregnated tapes (prepregs) manufactured from Kerimid 601 require solvent for room temperature tack, and the elimination of the solvent has caused problems. Without solvent, the K 601 prepreg is dry and boardy and although the opinion was not unanimous, this characteristic was considered to be a severe hindrance in processing. HX-580 and Hercules 4397 were reported to produce tacky prepregs without solvent, but these materials as well as a newer Kerimid, identified as K 353, have not yet been widely used.

There was little concern about the continued availability of these resins, assuming of course, a market for them. Resin and manufacturing specifications are either available or they can be developed without special problems. The fabrication of large-area structures with HX-580 does not appear to present any major new problems although there was some concern with other resins in the group due to the solvent requirements noted above.

The group was asked to express its opinions about the economic impact upon structures fabricated from these materials. How much more might a structure fabricated with bis-maleimide cost than an equivalent epoxy structure? The general consensus was that an additional cost of between 5 and 30 percent was reasonable.

The next resins discussed were the A-type/NASA materials which are generally imidized in-situ followed by addition reaction. Of particular interest were the PMR materials which are reported to be more appropriate to autoclaving processing than earlier versions of this family of resins. Tito Serafini of NASA/Lewis made an important contribution to the discussion of recent PMR's for which the panel was grateful.

Table 2 shows a performance matrix for these materials. Current performance levels attainable are shear strength of 12 ksi at 450°F after 1000 hours, 8 ksi at 600°F after 500 hours, and 4 ksi at 650°F after 50 hours. Potentially, these materials may provide 12 ksi shear strength at 600°F after 500 hours or at 550°F after 10 000 hours.

Earlier materials of this type such as P13N were not considered autoclavable. However, Serafini reported very early good data for PMR15 based on autoclave processing at 200 psi and 500°F. This raised the question as to the availability of equipment that provides this kind of pressure and temperature capability. Although there does not appear to be much of this type of equipment, several of the panel members did mention that they had equipment of this kind in sizes up to 5 ft by 15 ft. Serafini did note that lower pressure may be achievable.

Other problem areas may be critical heat-up rates and the volatility of methyl alcohol, which is currently used as the solvent for PMR15. About 15 percent solvent content is required in the prepreg to provide tack. Losses of solvent during the lamination of large parts may radically affect tack and other processability characteristics. Also, the material is not commercially available. The use of dimethyl formamide as the solvent for A-type resins

was also a cause for concern. Scheck reported that his company will not allow this solvent in his plant.

The cost premium associated with fabricating structures from these resins was estimated to be between 10 and 50 percent more than epoxies, with the 10 percent premium associated with compression molding.

Skybond resins were the next category to be considered. These resins are representative of the earliest polyimides, with both solvent and reactive volatiles liberated during cure and postcure. Table 3 summarizes the performance for this type of material. At 600°F, a shear strength of 8 ksi after 500 hours is a likely current level as well as 4 ksi at 700°F after 100 hours or at 450°F after 50 000 hours.

There was little positive speculation about future performance growth for these materials except possibly as to thermo-oxidative stability. In terms of such factors as availability, health hazards, or chemical resistance, these materials were considered to present few problems. The discussion was therefore primarily concerned with processing. This type of polyimide, among the best in performance, has also been the most difficult to process and the notorious reputation of polyimides has grown from experience with these materials.

Among the users at the meeting, the most experience was with Skybond 703 and 710. Scheck, Kollmansberger, and Maximovich all reported much variability in these materials. Sometimes they processed well into low-void-content composites, sometimes the same nominal material processed poorly. It was suggested that part of the variability was derived from inadequate tightness in the control of acid content in the solution provided by the manufacturers, although Markhart did not concur. Moisture presents another problem that can affect the prepregs due to hydrolysis with resulting precipitation according to Maximovich and others, and in flow behavior according to Petker.

Generally, the low-void-content composites prepared from these materials have required dry, boardy prepregs. With tacky prepregs, low-void content is even more difficult to achieve and its achievement is questionable with large-area parts. It was suggested by Scheck that 5-percent voids might be acceptable with these composites and both he and Yoshino considered 5- to 10-percent voids as within the state of the art. I did not concur, although I did not speak up. It was felt by the group that low-void-content composite structures fabricated with these materials could cost 100 percent or more than equivalent epoxy hardware. The meeting for the second day adjourned just prior to the completion of the discussion of these materials.

The Third Day

The third day began with the final comments on Skybond resin which have already been summarized. We then addressed ourselves to the thermoplastics represented primarily by the NR-type materials. Table 4 shows the performance of these materials as derived at the meeting, with current performance levels of 8 ksi at 500°F after 50 000 hours, 8 ksi at 600°F after 1000 hours, and 4 ksi at 700°F after 100 hours. A potential of 4 ksi at 600°F after 4000 hours may be achieved.

Much of this information for these materials was provided by Gibbs. He noted that the resin manufacturer also makes all of the starting materials and therefore has good control over resin manufacture. The resin will continue to be available and the commercial forms, such as NR150-B2, will be offered as constant formulation. These materials can be postformed by taking the composite beyond the glass transition temperature into the range of 750° to 850°F. Voids can be eliminated in this manner with pressures on the order of 200 psi and it may be possible to reduce voids at a lower pressure level. Continuing work suggests that autoclaving at lower temperatures and pressures may result in low-void content without the need for high-temperature postcompaction.

Gibbs also suggested that 7- to 10-percent voids do not have deleterious effects upon the thermal performance of these materials. He attributes this to their toughness. Maximovich, however, reported his experience

suggests that composites based on thermoplastics may be even more sensitive to voids than those based on thermosets. There was the feeling that these materials may offer the most promise among the polyimides for the best thermal performance, but there has not yet been sufficient experience with them to confirm this nor to state just how difficult to process and how reproducible these materials may be. For these reasons, we did not try to suggest the premium in cost that might attend the use of these materials.

The question of the status of adhesives for high temperature was still hanging, and this was discussed next. It appeared that FM34 is still the polyimide adhesive in most general use. It is a condensation type and both good and bad experiences were reported for it. As with the condensation composite resins, variability appears to be a problem with the adhesive, especially with large-area bonds under unusual manufacturing conditions. Politi did not think that formulations based on the addition polyimides would prove practical due to brittleness and therefore low peel strength. There was some optimism expressed that the thermoplastic polyimides may prove themselves capable of overcoming the deficiencies of other candidate high-temperature adhesive materials. It appears that the entire area of high-temperature polyimide adhesives requires a more thorough, more intensive study than was possible at this meeting.

It was getting close to the time to adjourn the meeting and it seemed that we needed a mechanism by which the panel could express not only a summation of what had transpired, but also the feelings that had developed about the future. I decided that possibly some spontaneous recommendations of the panel for NASA might provide this. I asked the panel to divide into two groups of four each (Winters had to leave and I thought it would be better if I played the role of observer in this last activity). Each group was asked to draw up a set of recommendations to NASA within about 15 minutes. I tried to separate the materials suppliers from the users, appointed a leader for each group, and asked that the recommendations be written. After receiving these two sets of recommendations, I thought it might be useful to combine the suppliers and users together and we went through the exercise again so that we ended with four sets of recommendations.

In turn, each group leader then presented the thoughts of his group. There was a surprising degree of commonality among the four, and I have summarized and reported them in Part A of this section.

The meeting adjourned. I left with a good feeling about the accomplishments of the meeting. Since then, there has been occasion for me to converse with a number of the panel members and each has appeared to express the same feeling.

NASA'S KEY ISSUES QUESTIONNAIRE 3

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Section 3
NASA'S KEY-ISSUES QUESTIONNAIRE

This section contains the three-page questionnaire prepared by NASA and distributed on 14 February 1975 to the 10 panel members, identified in Appendix A. By 14 March 1975 all of the responses to the questionnaire had been received by the McDonnell Douglas Program Office and were forwarded to the Composites Section of the Materials Branch at NASA-Langley Research Center. The responses to the questionnaire are summarized in general terms in Section 4 and are presented verbatim in Appendix A.

QUESTIONNAIRE

A. POLYIMIDE MATRIX AND ADHESIVE RESINS

1. Identify commercially available resins by:
   a. Designation and source — producer and/or supplier.
   b. Type — addition, condensation, thermoplastic.
   c. Form — liquid, solid, film, other.
2. Specify significant characteristics such as:
   a. Maximum use temperature for short, intermediate, and long-term exposures.
   b. Environmental effects of moisture, fuels, vacuum, radiation, etc.
   c. Possible health hazards.
   d. Processing limitations associated with producing the resin, manufacturing prepreg, laying-up and curing structural components.
   e. Compatibility with graphite fibers.
3. Identify experimental polyimide resins that are predicted to be commercially available within 5 years.

B. AVAILABILITY OF POLYIMIDE RESINS

1. Adequate or limited sources for raw materials.
2. Impact of Government regulations — OSHA, EPA, etc.
3. Influence of nonaerospace markets on the quantity and quality of resins available.
4. Effects of the changing state of the economy of producers.
5. Availability of current commercial polyimide resins in 5 years, 10 years, and 20 years.

C. MANUFACTURING PROCESSES AND EQUIPMENT

1. Describe the status of processes for:
   a. Producing resins — matrix and adhesive types.
   b. Manufacture of prepreg tape.
   c. Specifications for resins, prepreg, cured laminates.
   d. Quality control and nondestructive evaluation methods.
2. Describe the status of equipment required to:
   a. Manufacture resins, prepreg tape, large structural components.
   b. Nondestructive evaluation and quality control of large structural components.
3. Identify major problems associated with:
   a. Establishing adequate manufacturing specifications.
   b. Fabricating large structural components.

D. PROPRIETARY NATURE OF POLYIMIDE RESINS

1. Limitations on establishing adequate specifications for quality control.
2. Influence on long-term availability of resins — 5 years, 10 years, 20 years.

E. LIMITATION ON POLYIMIDE RESINS

1. Maximum potential use temperature.
2. Long-term durability.
3. Degree of difficulty in manufacturing large, complex structures.
4. Other.

F. NEW RESIN SYSTEMS

1. Identify potential replacements or competitors for polyimide resins.

2. Specific significant characteristics.

3. Assess the impact on availability of polyimide resins.

G. PRICE

1. Current and projected costs for:

   a. Raw materials.

   b. Resins.

   c. Prepreg.

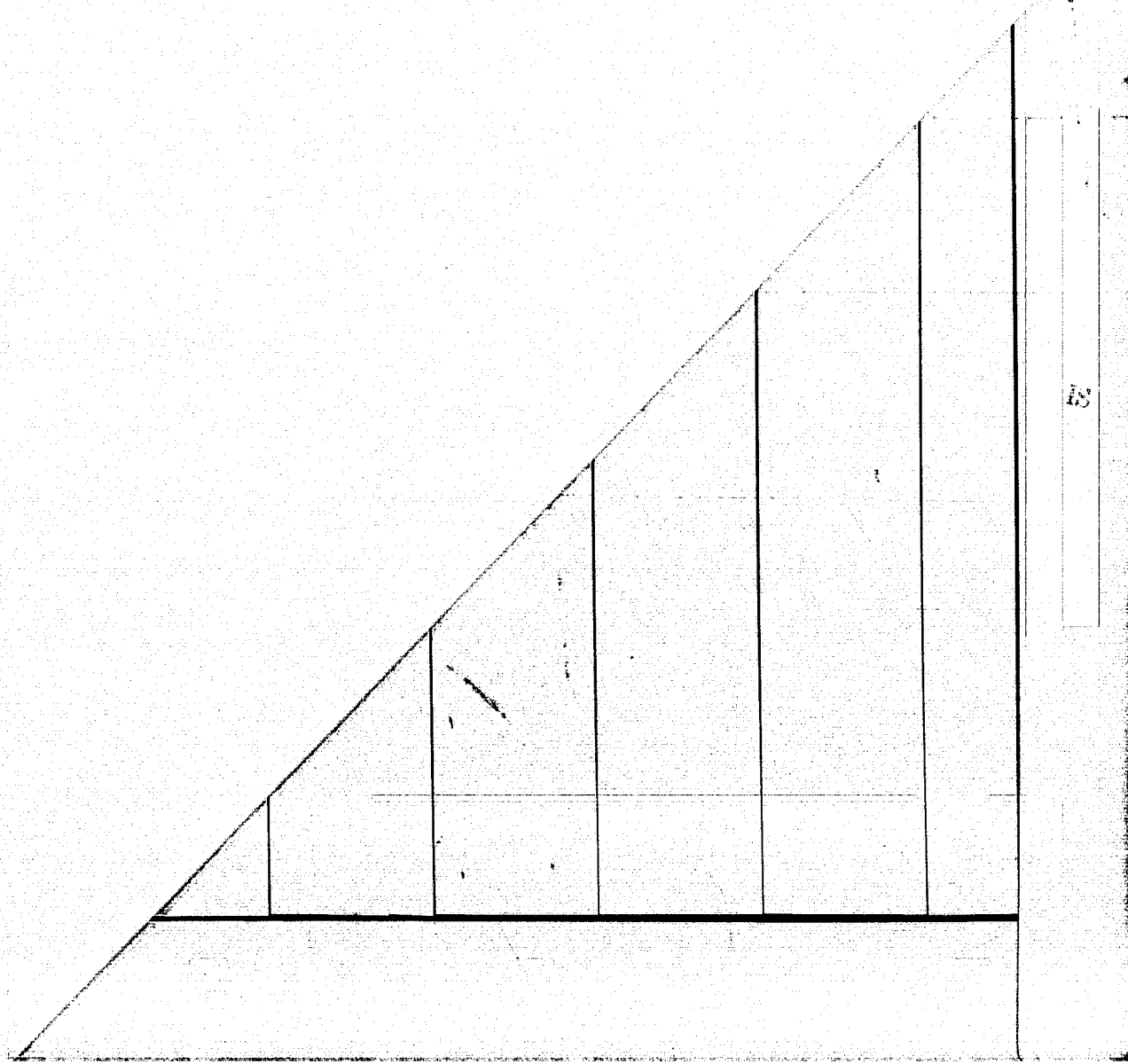
   d. Graphite-polyimide composites.

2. Identify major factors which will influence changes in costs and provide the rationale for predictions given under item G.1.

Issues A through G are stated to stimulate discussion of the polyimide technology and are not necessarily complete. Each panel member is requested to add other issues which have an impact on the technology. When discussing the issues, each panel member is requested to state his company's position. If the position stated differs from that of his company, the panel member shall clearly identify the difference and the background rationale.

In addition, each panel member is requested to provide a one-page double-spaced, typed SUMMARY of his discussion.

SUMMARY OF INDUSTRY RESPONSES TO THE QUESTIONNAIRE 4



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Section 4

SUMMARY OF INDUSTRY RESPONSES TO THE QUESTIONNAIRE

This section summarizes the responses of the 10 members of the industry working group to the questionnaire presented in Section 3. By necessity, this summary is brief and general, limited primarily to the points of agreement in the answers because the collective knowledge of those participating in the conference is both comprehensive and detailed. For this reason, the reader interested in the extensive details and the variations in the individual responses is referred to the documents collected in Appendix A.

SUMMARY OF INDUSTRY RESPONSES TO NASA QUESTIONNAIRE
(Compiled by MDAC)

	Question	Response
A. 1	Identify polyimide matrix and adhesive resins	• Monsanto Skybond 700 series resins — condensation reaction available in solutions
		• DuPont Pyralin 4701/4707 resins — condensation reaction available in solvent solutions
		• DuPont NR-150 resins — thermoplastic after imidization available in solvent solutions
		• Rhodia Nolamid 605 resins — condensation reaction available in solvent solutions
		• Rhodia Kerimid 601 resins — addition reaction available in solvent solutions
		• CIBA-GEIGY P13N resins — addition reaction available in powder and solvent solutions
		• Upjohn Polyimide 2080 resins — a thermoplastic resin available in powder and solvent solutions
		• Hexcel HX-580 or F-178 resins — available in film
A. 2	Specify significant polyimide resin characteristics such as use temperature with time, environmental effects, health hazards, processing limitations, and compatibility with graphite	• Condensation reaction types vary from use at 500°F for long periods (over 10 000 hours) to 1000°F for short times (seconds or minutes). Thermoplastic types are limited to the 450° to 650°F range. Addition reaction types are limited to temperatures not exceeding 450°F; for very long periods, the upper limit is about 400°F.
		• All types have adequate resistance to moisture, salt spray, fuels, vacuum, etc.; strong alkalis and paint strippers are the exception. Most environmental problems have been associated with the bondline rather than with the resin itself. One problem which may occur is galvanic corrosion between the metal and graphite-resin system when exposed to salt solutions.

SUMMARY OF INDUSTRY RESPONSES TO NASA QUESTIONNAIRE (Continued)
(Compiled by MDAC)

Question		Response
		• Skin contact should be avoided in handling all types. Adequate ventilation should be provided when handling solvent solutions and during imidization processes.
		• Curing of condensation reaction resins produces volatiles which must escape if a low-void-content composite is to be fabricated. This necessitates the use of fabric bleeder systems, two-stage bonding, and/or perhaps vent holes to aid in removal of the volatiles when large-area structures or bonds are manufactured. Satisfactory cure cycles for condensation reaction polyimides are in the 350°F and 100- to 200-psi range; however, postcure cycles above the intended use temperature are required, with lengths in excess of 100 hours for some resin systems. Forming of shaped structures from thermoplastic sheet materials requires temperatures near the glass transition temperature. Generally, conventional processing techniques can be used with addition reaction resins although the pressures required to fabricate low-void-content composites may be as high as 600 psi for some resins.
		• All polyimide resins appear to be compatible with graphite fibers.
A. 3	Identify polyimide resins that may be commercially available within five years	• CIBA-GEIGY — A-2 thermosetting polyimide (replacement for P105A)
		• DuPont — experimental NR-150's
		• Hercules — 4397 addition resin
		• Monsanto — an experimental polyimide varnish which cures to the most oxidative, thermally stable polyimide known.
		• Hughes — HR-600
		• NASA-LeRC — PMR

SUMMARY OF INDUSTRY RESPONSES TO NASA QUESTIONNAIRE (Continued)
(Compiled by MDAC)

	Question	Response
B.	Availability of polyimide resins	
B.1	Sources for raw materials	• All of the raw materials for commercial resins now appear to be available in sufficient quantity to meet projected needs.
B.2	Impact of Government regulations	• The products are manufactured without air or water pollution. Compliance with regulations should pose no problems.
B.3	Nonaerospace market influence on the quantity/quality available	• Present and new commercial applications in the nonaerospace market should keep the quality and quantity of resins readily available for aerospace applications.
B.4	Effects of the changing economy on producers	• If the demand grows, there should be no effect on the availability of the resins.
B.5	What is the prediction for current resin availability in 5, 10, 20 years	• The current resins should be available; however, improved versions should also be available in future years. An increase in the use of the resins is expected in the near future.
C.	Manufacturing processes and equipment	
C.1.a	What is the status of processes for producing the resins-matrix and adhesive types	• The processes are well defined and the systems are being produced on a routine basis. Scale-up to large-volume equipment has been satisfactorily achieved.
C.1.b	What is the status of prepreg tape manufacturing	• Several companies manufacture polyimide resin prepreg tapes. However, there is continuing debate on the adequacy of the specifications.

SUMMARY OF INDUSTRY RESPONSES TO NASA QUESTIONNAIRE (Continued)
(Compiled by MDAC)

Question	Response
C.1.c Specifications for resins, prepreg, cured laminates	• Specifications such as solids content, solution viscosity, density, T_g (e. g., transition temperature from glassy to rubbery behavior) exist. These are not adequate, and additional specifications are required before the systems can be used in production of primary structural components for aerospace vehicles.
C.1.d What about quality control and non-destructive evaluation methods	• Quality control methods currently used include QC-IR scan; thermal gravimetric analysis (weight loss as a function of temperature), and differential thermal analysis; nondestructive evaluation is carried out by x-ray and ultrasonic inspection. However, improvements in all methods are needed.
C. 2 Describe the status of equipment required to:	
C.2.a Manufacture resins, tape, and large structural components	• Sufficient equipment exists for the manufacturing of resins and tapes. Most aerospace companies have autoclaves capable of high pressures and temperatures. The requirements in cure temperatures and pressures will limit the size of components. However, structural components 4 by 5 feet and larger can be made, although no production program involving the fabrication of large, high-quality structural components from graphite/polyimide or utilizing significant large-area or sandwich polyimide bonding has been completely successful to date.
C.2.b Effect quality control and nondestructive evaluation of larger structural components	• Many companies use C-scan equipment and end-tag specimens to ensure the quality of fabricated parts. Nondestructive testing can be used to detect various types of flaws. Current techniques, however, are not wholly adequate.

SUMMARY OF INDUSTRY RESPONSES TO NASA QUESTIONNAIRE (Continued)
(Compiled by MDAC)

Question		Response
C. 3	Identify major problems associated with:	
C.3.a	Establishing adequate manufacturing specifications	• No major problems.
C.3.b	Fabricating large components	• The removal of volatiles during cure and the future requirements for larger, higher-pressure and higher-temperature presses and autoclaves than are now presently available. • Another problem is the handling and drapability of highly B-staged, nontacky polyimide prepreg for contoured parts. • Maintaining cleanliness and high-quality surface treatments for bonded structure.
D.	Proprietary nature of polyimide resins	
D. 1	Limitation on establishing adequate specifications for quality control	• The composition of each resin is of course proprietary. It is generally believed that this should not be a significant obstacle to providing satisfactory quality control or adequate specifications.
D. 2	Influence on long-term availability of resins (5, 10, 20 years)	• Answers from "no problems" to a profound influence (see individual responses to this question).

SUMMARY OF INDUSTRY RESPONSES TO NASA QUESTIONNAIRE (Continued)
(Compiled by MDAC)

	Question	Response
E.	Limitation on polyimide resins	
E. 1	What is the maximum potential use temperature	• Answers varied from 500° to 1200°F for condensation reaction types. This is a difficult question to answer, since it depends on so many factors such as resin type, time-in-use, the environment, and the sustained load levels. (See detailed answers.)
E. 2	Long-term durability	• Most companies consider polyimides to be the most stable and environmentally resistant of all resins. However, there is very little field experience in structural life or refurbishment of damaged structure.
E. 3	Difficulty in manufacturing large, complex structures	• (See individual responses in Appendix A.)
F.	New resin systems	
F. 1	Identify potential replacements or competitors for polyimide resins	• American Cyanamide-Polyphenylquinoxilines, not available in commercial quantities, as now synthesized and priced extremely high. • Monsanto — a dozen types are identified in the Monsanto response (see Appendix A).
F. 2	Specify significant characteristics	• Many of the advanced research resins are much tougher than the commercially available polyimides. They could result in high-temperature operating systems which possess high metal-to-metal sandwich peel characteristics.
F. 3	Assess the impact of new resin systems on the availability of polyimide resins	• It is unlikely that the new resins would have any impact on the availability of Skybond polyimides.

SUMMARY OF INDUSTRY RESPONSES TO NASA QUESTIONNAIRE (Concluded)
(Compiled by MDAC)

Question		Response
G.	Price	
G. 1	Current and projected costs for raw materials, resins, prepreg, and graphite polyimide composites	• Prices vary by type and by quantity, i. e., whether for R&D programs or for production uses. (See individual answers in Appendix A.)
G.2	Identify major factors which will influence changes in cost	• Major factors influencing cost are and will be: raw material prices, depending on petroleum availability and its cost, and conversion factors which depend on labor rates, production volume, and the cost of energy. Actual values cannot be predicted at this time. Prices may increase but on the other hand they may drastically decrease if the applications increase.
	Summary of your company's or an individual's position on graphite polyimide technology	• Five out of 10 responders addressed themselves to this item (Appendix A).

INDUSTRY RESPONSES TO THE QUESTIONNAIRE A

Appendix A
INDUSTRY RESPONSES TO THE QUESTIONNAIRE

The 10 responses presented in this appendix were prepared from 14 February to 14 March 1975. They are unedited and are presented in alphabetical order by company.

American Cyanamid	Mr. R. Politi
CIBA-GEIGY	Dr. S. S. Hirsch
Composites Horizons	Mr. I. Petker
DuPont	Dr. H. Gibbs
General Dynamics	Mr. W. G. Sheck
McDonnell Douglas	Mr. R. Kollmansberger
Monsanto	Dr. A. H. Markhart
Rockwell International	Mr. S. Yoshino
TRW Equipment	Mr. W. E. Winters
Whittaker	Mr. M. G. Maximovich

AMERICAN CYANAMID RESPONSE

AMERICAN CYANAMID RESPONSE

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ASSESSMENT OF GRAPHITE-POLYIMIDE COMPOSITES TECHNOLOGY

The American Cyanamid Company has not been active in the development or production of graphite polyimide prepregs or of polyimide resin compositions for the impregnation of graphite. Our major area of expertise has been in the development and production of polyimide based adhesives and primers for aerospace applications and, we are, therefore, limiting our discussion to this phase of polyimide technology.

A. POLYIMIDE (PI) MATRIX AND ADHESIVE RESINS

1. Commercially Available Resins

a. Skybond Resins - Monsanto: A series of condensation reaction resins available as solvent solutions.

b. Pyralin Resins - DuPont: A series of condensation reaction resins available as solvent solutions.

c. NR-150 Resins - DuPont: A series of resins that remain thermoplastic after imidization. Available as solvent solutions.

d. Nolamid 605 - Rhodia: A condensation reaction resin available as a solvent solution.

e. Kerimid 601 and 353 - Rhodia: Addition reaction resins supplied as solvent solutions.

f. P-13N - Ciba-Giegy: An addition reaction PI resin available as a solid powder and as a solvent solution.

g. Polyimide 2080 - Upjohn: A thermoplastic polyimide available both as a solid powder and as a solvent solution.

2. Significant Characteristics

a. Maximum use temperature for condensation reaction resins - The most stable resins of

2. a. this type show good strength retention after short time exposures (seconds or minutes) to temperatures in excess of 1000°F. They are resistant for moderate periods of time to temperatures in the 600 to 800°F. range. The best resins of this type will resist temperatures in the 500°F. range for periods exceeding 40,000 hours.

Thermoplastics - Depending on melting point, are limited to applications where temperatures will not exceed 450 to 650°F. Long time aging characteristics are generally similar to condensation reaction resins.

Addition Reaction Resins - Generally limited to applications where temperatures will not exceed 450°F. For applications involving very long time aging, upper limit is probably about 400 to 425°F.

b. Environmental Effects - All types appear to have adequate resistance to moisture, salt spray, fuels, anti-icing fluids, hydrocarbons and vacuum. Most exposure problems are related to porosity in the bond line rather than any inherent weakness in the resin.

c. Possible Health Hazards - Skin contact should be avoided in handling all types. Adequate ventilation should be used when handling solvent solutions. Good ventilation should be provided during the imidization process, particularly if the system is stabilized with an arsenic compound.

d. Processing Limitations

Condensation Reaction Resins: Should be "cured" using vacuum to facilitate the removal of solvent and water formed during the imidization process. When large area bonds are being made, prolific use of fabric bleeder systems, two stage bonding and use of vent holes will all help facilitate the release of volatiles.

Thermoplastic Resins: Must be fabricated using temperatures that substantially exceed the service temperature.

Addition Reaction Resins: Can generally be processed using conventional techniques.

e. Compatibility with Graphite Fibers - All types appear to be compatible with graphite.

B. AVAILABILITY OF PI RESINS

1. All of the commercial resins appear to be available in sufficient quantities to meet projected usage.

C. MANUFACTURING PROCESSES AND EQUIPMENT

3. Major Problems

b. Fabricating Large Structural Components - With the condensation reaction polyimides the major problem is obtaining complete release of volatiles and void-free structures. With the thermoplastic polyimides the major problem is that the fully imidized resin is rigid and lacks drape so that it will not conform to contours during lay-up.

E. LIMITATION ON PI RESINS

1. Maximum Potential Use Temperature

a. Condensation Reaction Types - 1000°F. to 1200°F.

b. Thermoplastics - 600°F. is a practical limit

c. Addition Reaction Types - 450°F. at present; potential unknown.

3. Degree of Difficulty in Manufacturing Large Structures - It is most difficult for condensation reaction types because of volatile problem

E. 3. and thermoplastic types because of lack of drape and tack.

F. NEW RESIN SYSTEMS

1. Polyphenylquinoxilines - Resins of this type have been synthesized which are much tougher than any of existing polyimides. In the adhesive area this could result in high temperature systems possessing high metal-to-metal and sandwich peel. The intermidiates used in the synthesis of PPQ's are not available in commercial quantities and for this reason the price is extremely high.

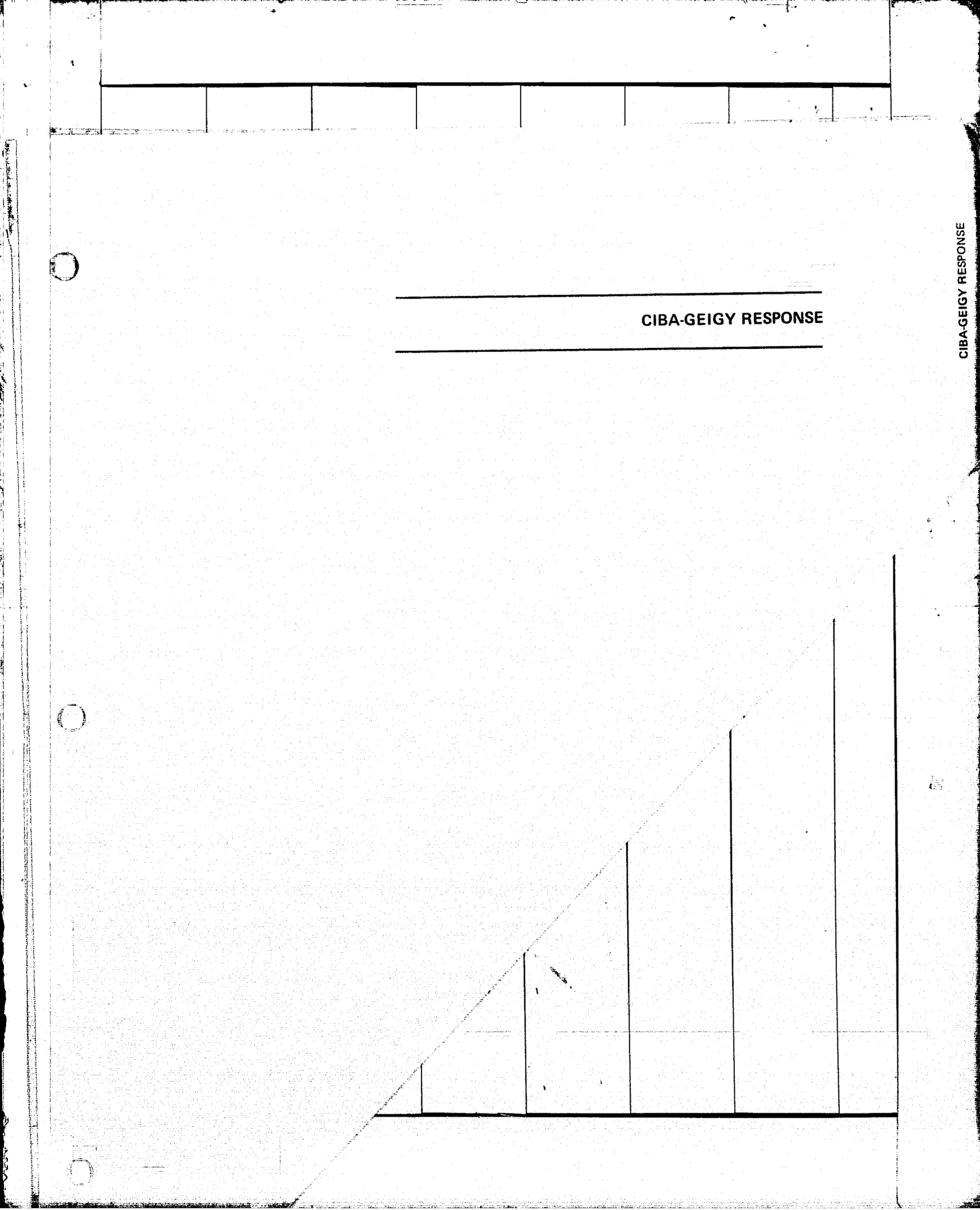
SUMMARY

Commercially available polyimides fall into three classes (1) Condensation Reaction Resins (2) Thermoplastics and (3) Addition Reaction Resins. Condensation Reaction Resins are available having excellent short term strength at temperatures in excess of 1000°F. and good strength retention after long time aging at temperatures up to 600°F. They are difficult to process because of the volatiles evolved during the imidization step which necessitates the use of venting and bleeder systems when large area bonds are being made.

Thermoplastic Resins are available having good initial strength and strength retention after long time aging at temperatures up to 650°F. These resins may be processed in the fully imidized state. However, when in the imidized state they are boardy and will not conform to contours. In addition, high fabrication temperatures are required (650°F. to 750°F.).

The Addition Reaction polyimides currently available are capable of withstanding long term exposures to temperatures in the 400°F. to 450°F. range. They are the easiest type of PI to process, since no volatiles are evolved during the cure and processing temperatures are moderate.

CIBA-GEIGY RESPONSE



SUMMARY - GRAPHITE/POLYIMIDE TECHNOLOGY ASSESSMENT

CIBA-GEIGY Corporation
Ardsley, New York 10502

Respondent: Dr. S. S. Hirsch

CIBA-GEIGY Corporation supplies P13N polyimide resin to industrial and aerospace customers. Our Resins Department is committed to the high performance thermoset market; the present and foreseen product mix includes thermally stable candidates. Recently added were Xylok resins, a 500°F (long term) performing system with handling characteristics of phenolics. In R & D, the A2-alternate aromatic polyimide program is well advanced. This is a volatiles-free 400°F-curing candidate for service to 550°F. Another mature project centers about the NCNS resin family, volatiles free matrices for service to 500°F. In addition are a number of programs, in the USA and abroad, aimed at the 400-525°F market in multiple end uses.

Our company considers cost-performance-effectiveness uppermost in developing resins for this market. "Exotic" synthetic approaches and difficult-to-process candidates are shunned. We recommend NASA choose goals that stop short of "squeezing" the ultimate thermal limit from the technology. As service temperatures increase, so do processing constraints - an appropriate balance should be sought.

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Response to Polyimide Questionnaire by

CIBA-GEIGY Corporation

Ardsley, N.Y. 10502

Respondent: Dr. S. S. Hirsch
Manager, Market Research
& Business Development
Resins Department

A. POLYIMIDE (PI) MATRIX AND ADHESIVE RESINS

1. Identify commercially available resins by:

a. Designation and source - producer and/or supplier - CIBA-GEIGY Corporation supplies P13N polyimide resin from production facilities in Toms River, New Jersey through the Resins Department in Ardsley, New York. P105A, a modified version of this resin, is no longer offered due to unavailability of one of the key intermediates - thiodianiline.

b. Type - addition, condensation, thermoplastic - P13N polyimide is an addition cure aromatic polyimide which eliminates no volatiles during molding and processes to void-free parts.

c. Form - liquid, solid, film, other - P13N polyimide is supplied as a 40% varnish and as neat powder for formulating molding compounds. The powder, being

already B-staged, cannot be redissolved to reconstitute varnish.

2. Specify significant characteristics such as:

a. Maximum use temperature for short, intermediate and long-term exposures - P13N polyimide, after proper post cure, can easily be exposed to 700-800°F for short periods, to 600°F for intermediate periods (250 hours) and at 550°F for long term exposure (1000 hours).

b. Environmental effects of moisture, fuels, vacuum, radiation, etc. - P13N polyimide is relatively unaffected by moisture fuels or vacuum. However, the resin should not be exposed to strong base.

c. Possible health hazards - There are no known health hazards connected with handling P13N resin; (this is not a warranty that none exists); however, DMF solvent used in the varnish form should be handled with care. Precautions for using DMF are well known and may be obtained from the solvent manufacturer, duPont Company.

d. Processing limitations associated with producing the resin, manufacturing prepreg, laying-up and curing structural components - No limitations to producing the resin have been uncovered to date although manufacture of varnish is simpler than powder resulting in lower cost for the former, at least at present production levels. Prepreg manufacture also is straightforward,

control of B-staging being facile. P13N is easily handled as a tacky prepreg containing approximately 10% solvent and thus is layed up without difficulty. Cure, however, requires rapid heat-up over the temperature range 400°F to 550°F (550°F is the final cure temperature), this 150° range being traversed during approximately two minutes maximum. Slower heating rates generally result in incompletely consolidated parts. However, we recently learned NASA has been achieving success by modified autoclave procedures which do employ slower heat-up rates. High heating rates normally are achieved by employing preheated molds and limiting the thickness of sections to approximately 1/4". Accordingly, the ordinary vacuum bag/autoclave procedure is not used with P13N, matched metal molding being more suitable.

e. Compatibility with graphite fibers - P13N is entirely compatible with graphite fibers.

3. Identify experimental PI's that are predicted to be commercially available within 5 years - CIBA-GEIGY Corporation has in the advanced research stage an aromatic thermosetting polyimide designated A2-alternate which cures volatiles free by an addition process at 400°F. The resin is soluble in low boiling solvents. We are optimistic concerning the potential for this candidate. While A-2 alternate is viewed

as the P105A (improved) replacement candidate, attempt is also being made to find a direct substitute for thiodianiline. Our company also has for sale and under development a number of resins for service temperatures between epoxies and aromatic polyimides (see Section F).

B. AVAILABILITY OF PI RESINS

1. Adequate or limited sources for raw materials - P13N polyimide is synthesized from methylenedianiline, BTDA, and nadic anhydride. The solvent is DMF. No availability limitations are foreseen for either MDA or DMF. BTDA is available from a single source (Gulf Oil Corporation). Nadic anhydride, while not a huge volume commercial chemical, appears to be available in the quantities anticipated for polyimide production.

2. Impact of government regulations - OSHA, EPA, etc. - As stated above, DMF solvent used in P13N varnish should be handled with care and could become subject to regulations being proposed and enacted for the handling of industrial solvents. Toxicity restrictions for certain aromatic diamines (e.g. MOCA and benzidine) are not applicable to methylenedianiline used to formulate P13N.

3. Influence of non-aerospace markets on the quantity and quality of resins available - P13N polyimide is being supplied both to the aerospace and industrial markets. We do not anticipate this dual end-use to result in any

special influence on either the quantity or quality of these resins for aerospace applications.

4. Effects of the changing state of the economy of producers - High performance polyimides are a relatively small volume product for a major corporation such as CIBA-GEIGY. Accordingly, we do not anticipate abberations as a result of economic forces. Our Resins Department is committed to marketing high performance specialty polymers including those of the high temperature class.

5. Availability of current commercial PI's in 5 years, 10 years, 20 years in the future - At present we see no reason for P13N polyimide not to be available over the stated time period, unless, of course, it becomes superseded by an improved version, and our customers agree to employ the latter for their requirements.

C. MANUFACTURING PROCESSES AND EQUIPMENT

1. Describe the status of processes for:

a. Producing resins - matrix and adhesive types - P13N laminating varnish is fully commercial in our plant.

b. Manufacture of prepreg tape - CIBA-GEIGY Corporation does not manufacture prepreg tapes but supplies P13N varnish to all major producers of this product form, virtually all of whom are capable of using this resin to produce a quality product.

c. Specifications for resins, prepreg, cured laminates - The specifications for P13N polyimide laminating varnish are:

Solids content,W/O	38-42
Color	Amber
Solvent	Dimethylformamide (DMF)
Viscosity at 25C,cps	250-350
Specific gravity	1.09-1.10
Acid number, approx.	3.80
Wt/gal,lbs.	9.1

d. Quality control and nondestructive evaluation methods - Quality control is a proprietary matter of our production department. Non-destructive evaluation methods do not apply to the resin itself and are best commented upon by fabricators.

2. Describe the status of equipment required to:

a. Manufacture resins, prepreg tape, large structural components - Both resin and prepreg tape manufacture employing P13N are fully commercial processes. At present, large structural components from P13N are prepared with some difficulty due to the unsuitability of the vacuum bag/autoclave process for this resin.

b. Nondestructive evaluation and quality control of large structural components - Not applicable to the resin producer.

3. Identify major problems associated with:

a. Establishing adequate manufacturing specifications - There are no major problems associated with manufacturing specifications.

b. Fabricating large structural components - As noted above, large structural components fabricated from P13N resin must be heated rapidly between 400°-550°F. The NASA personnel at this meeting should be able to comment on recent improvements they have made in this connection.

D. PROPRIETARY NATURE OF PI RESINS

1. Limitations on establishing adequate specifications for quality control - P13N polyimide was developed under Government contract and accordingly, has few proprietary limitations. We foresee very little difficulty on this count. For our newer systems such as A-2 alternate, we anticipate no difficulty in establishing adequate specifications; certainly not because they are proprietary products.

2. Influence on long-term availability of resins - 5 years, 10 years, 20 years in the future - From the resin manufacturer's point of view, we do not see the proprietary nature of products becoming an influence on long term availability.

E. LIMITATION ON PI RESINS

1. Maximum potential use temperature - Of course, this depends

upon time at temperature, but speaking from a balanced point of view, we view 600°F as being a maximum realistic potential for long-term use, particularly when considered together with the processability question. Please see my comments at the end of the questionnaire for an elaboration of this topic.

2. Long-term durability - This question is not entirely clear but we are not aware of any particular shortcomings of polyimide resins as concerns long-term durability.

3. Degree of difficulty in manufacturing large complex structures - This of course is the real problem area. There exists a trade-off in level of thermal stability achievable and ability to manufacture a large complex structure economically. I will comment on this point at the end of the questionnaire and plan to devote my presentation and some of the discussion period to this very key question.

4. Other - It should be realized market potential for resins with service temperatures between 400-525°F is considerably greater than that between 525-600°F+. This means resin producers will (rightly) tend to direct the majority of attention to developing candidates with greatest business promise. In turn, this can be expected to result in reducing effort committed to development of truly cost-effective candidates for complex-shaped, large, structural parts for service in the 525°F+ region. This "fact of life"

is another area I plan to discuss during the meeting. Let me state here that much can be said for not trying to squeeze every bit of thermal performance theoretically possible out of organic resins since an unacceptable penalty almost certainly will have to be paid in development and product cost, and most especially in processability. Rather, the best balance of thermal stability, facile processing and modest cost should be sought.

F. NEW RESIN SYSTEMS

1. Identify potential replacements or competitors for PI resins - There are dozens of organic resin svstems with the thermal properties of polyimides which at first glance could be considered potential replacements. However, upon careful examination, we find it unlikely based upon current costs and state of the art that effective competitors for the temperature range 550°F and above will surface, at least if forces of the marketplace are determining. We have presented technical papers on several occasions supporting this view and I will be pleased to repeat the argument at the seminar. For the temperature range 400-525°F there are many potential replacements for, and competitive materials to polyimides. First, of course, are the non-aromatic maleimide resins. Candidates of this type already in the field only scratch the surface of what is possible with this versatile system. CIBA-GEIGY Corporation has recently

acquired exclusive rights in North America to the Xylok resin family developed by Albright & Wilson in the United Kingdom. These resins, which are the condensation products of aralkyl ethers with phenols handle and cure exactly like phenolics, are low in cost and are suitable for long-term use at 500°F. The market already is substantial in other countries. A modified version of these resins, Xylok 234C, is very epoxy-like (vs. phenolic-like) and is suitable for long-term use at 425°F. This latter system cures without volatiles elimination. Another CIBA-GEIGY system of which NASA is already aware, NCNS resin, is a developmental addition cure system suitable for long-term use up to 500°F. Dr. Kray's recent paper concerning this novel resin family recently won Best Paper Award at the February SPI meeting, which adds to our already-existing encouragement for this polymer class. A variety of proprietary high temperature polymer systems primarily designed for the temperature region 400-525°F are currently under development in our laboratories. End uses foreseen are structural and electrical laminating, molding, adhesives, casting, foams, encapsulation, enamels and impregnation.

2. Specific significant characteristics - Answer is already given in Item F 1.

3. Assess the impact on availability of PI resins - As stated above, we believe the principal impact of new systems on

availability of PI resins will be the greater market potential of cost-effective and easy to process candidates in the 400-525°F region. This can be expected to divert attention from the 525-600°F+ region in which NASA may have greater interest.

G. PRICE

1. Current and projected costs for resins - The current price of polyimide solids in P13N varnish is $6.87/lb. Xylok resins are being introduced to the market between $3.50 - $4.20/lb. on a solids basis. Our Legal Department advises no discussion of price beyond statement of current published list is permissable in any medium where competitors participate. Price can be discussed with NASA via the usual vendor-customer relationship, but not as part of this coordinated program involving competitors.

2. Identify major factors which will influence changes in costs and provide the rationale for predictions given under item G.1. - A major factor which will influence the cost of high temperature resins is any requirement for employing non-commercial, difficult to synthesize intermediates since raw materials for aromatic resins such as polyimides are of fairly high cost even in simple cases. Any requirement for custom synthesis can cause costs to balloon, especially if volumes are modest. Generally speaking, a move away from polyimides toward, for example, polyquinoxalines, poly-

benzimidazoles, etc. will result in high costs simply because the dianhydrides employed in polyimide synthesis are the only inexpensive tetrafunctional aromatic monomers, and at least one tetrafunctional moiety appears to be required for every resin system offering very high temperature capability. However, we strongly believe processing considerations will far outweigh resin prices (within reasonable limits) as the composites age develops. Processability - this means low temperature fabrication, forgiveness during molding, freedom from volatiles evolution, employment of an easily removable solvent and lack of thermoplasticity, among others - are the factors first to be considered when developing any new high performance resin system intended primarily for use in composites. Please see my supplementary comments for elaboration.

SUPPLEMENTARY COMMENTS

The comments in this section are my own, but they reflect in considerable measure the opinions of my CIBA-GEIGY colleagues. We have engaged in high temperature polymer research and development both in the United States and Europe for more than seven years at a significant manning level and, further, have interfaced with most other participants in this technology, on a technical and vendor-customer basis. In addition, we share the benefit of having witnessed parallel developments which are instructive. If there is

one key point I would like to convey at this conference, it is the following:

DO NOT ATTEMPT TO SQUEEZE THE ULTIMATE LIMIT OF PERFORMANCE OUT OF THE TECHNOLOGY

The reason is simple. The point of diminishing return is reached well before the ultimate performance limit. Recall the SST program. A speed objective was chosen which resulted in very high skin temperatures (as I recall approximately 450°F). This, in turn, led to material and process requirements very difficult to achieve at reasonable cost which, in my opinion, contributed to ultimate withdrawal of support. Would not a more modest speed objective have resulted in strikingly lower skin temperatures and, in turn, permitted cost-effective solutions to the materials problem?

The same point can be made concerning the entire field of advanced composites and high temperature resins. Surely, many of these resins are capable of withstanding 600°F (or even higher) for substantial periods, but finding a system of facile processability into large, complex structures while retaining this level of thermal stability has proved very elusive. Let's look at what we have. There are condensation resins which offer the desired thermal stability but possess volatiles elimination and void problems which never seem to go away. Then consider the addition cure systems which seem invariably to result in compromised thermal stability and sometimes processing difficulties. The other

major family is the thermoplastic polyimides, which, in order to retain physical properties at say, 600°F requires choosing a candidate of sufficiently high T_g that processing at extremely high temperatures is necessitated. As noted earlier in this paper, much of industry's attention is being diverted toward more modest temperature goals with greater business potential (for example, Xylok, NCNS, maleimides, polyphenylene sulfide, amide-imides, etc.). I would like to recommend, and throw open for discussion the proposition that 600°F long-term performance, while achievable technically, may represent too high a percent of the ultimate attainable from organic systems to have high potential for cost-effectiveness. The ultimate likelihood of success with graphite composite structures at elevated temperatures will be considerably enhanced if the design goal lies between 500-550°F. Then, a very good chance of developing both cost-effective resins and cost-effective processes will exist. Furthermore, and extremely important, the likelihood of realizing this goal during a reasonable time frame (for example, at least semi-commercialization within the next 5-7 years) will be greatly enhanced. I will be particularly disappointed if the graphite/polyimide composite age fails to come about during our careers simply because we - all of us - will have chosen a goal which "bites off more than we can chew".

COMPOSITES HORIZONS RESPONSE

FEB 28 '75

DISCUSSION OF GRAPHITE-POLYIMIDE COMPOSITES

By: Ira Petker , Composites Horizons

SUMMARY

My direct experience with Skybond 703, P13N and Keramid 601 polyimide resins in composites is described. We have prepared high-quality, very low void content composites from all of these materials with excellent high temperature mechanical properties. These three resins are representative of the broad variation in the processing behavior and thermal capability of current polyimides. These materials are discussed from the point of view of a Composites Materials Engineer. The perspective is somewhat different from usual in that the organization of these materials is based on their processing behavior, rather than their chemistry. The advantages, disadvantages and limitations of each as composite materials are discussed. A methodology for extrapolating these materials to other polyimides is inferred.

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DISCUSSION OF GRAPHITE-POLYIMIDE COMPOSITES

By: Ira Petker , Composites Horizons

I will address myself in this discussion of polyimide (PI) resins primarily to what I know personally, from my own experience, as a Composites Materials Engineer. In this capacity I am concerned with such questions as "What is a good composite?", "How will a material perform as a composite?", and "Can a good composite be made from a given material and How?". I believe that an effective Composites Materials Engineer must know something about polymer chemistry, especially when it comes to rheology and reactivity, he must know something about mechanical engineering, especially stress and strain, he must know something about physics, about tooling and other disciplines. However, he should know about these things in relation to the kinds of questions I stated above.

I have often thought that a major obstacle to the evolution of Modern Composites has been a tendency for many of the workers in and contributors to the Technology, to look at it as being composed of an extremely high number of unrelated, unique, non-interdependent qualities orcharacteristics of materials. I think that this has been a major problem in the rate of growth of applications for polyimides. Later I will relate an experience of this tendency and suggest the confusion it breeds. Polyimides also have been confused

by a tendency to cover up the differences between them. To me it is confusing to describe both Skybond 703 and Keramid 601 as 'polyimides'. To me Skybond 703 and Keramid 601 convey as much difference, not sameness, as the terms 'epoxy and polyimides'. Skybond 703 and Keramid 601 are not within the same class of materials. To me they are more different as materials than are Keramid 601 and a resin system called 58/68R from my Aerojet days. (58/68R is an epoxy resin system made from Epon 828, Epon 1031 and methyl-nadic anhydride). I will amplify this position in my presentation.

My first experience with polyimide resin occured in 1967. I was at Aerojet and was appointed Program Manager midstream in an Air Force Materials Laboratory contract to develop materials and processes for boron composites. The direction of the program was changed about that time by the Air Force from an emphasis on epoxies toward developing high temperature boron composites. The highest temperature regime I had worked in prior to that had been about 300° F and now the Air Force wanted me to tell them how high they could go in temperature, and worse than that, how soon.

I scurried through the literature, spoke to many people and arrived at the conclusion that Skybond 703 had as good a

chance to make it to about 600° F structurally as anything else around. We chose to work with it exclusively. I felt that if we could make a good composite with this polyimide, then we probably had a good shot at making it with almost any other polyimide. It also coincided that for the potential users of high temperature boron composites, reentry people and jet engine people, 600° F was a very attractive operating temperature.

I came to the conclusion almost immediately, when we were given the problem , that the only ghost of a chance that we had to be successful quickly was if we could make polyimides process like epoxies, and then if polyimides did behave just like epoxies within a composite. My major prior experience in composites had been with epoxies and polyesters and a bit with phenolics and silicones, but I found many similarities between these polymers. I anticipated (hoped for) similar behavior by the polyimides.

We thought we had learned that almost any epoxy resin system that could be made into a void-free composite would also be a structural composite if the resin were strong. We also had the impression from epoxies that strength at temperature for a composite was totally dependent upon the strength of the matrix at that temperature. We extrapolated with polyimides to 600° F what we had observed with epoxies at 300° F. We set about,

then, to try to make a void-free composite with Skybond 703 and boron fiber.

We were in close contact with the Air Force Technical Monitor, Ed Jaffe, and after about 3 months of work he felt that we had made important progress. He organized a small meeting, limited to developers and producers of polyimides, to discuss with them what we had observed.

At that time the best polyimide composites were quoted at 22 v/o voids. We felt that we had to get this number down significantly or we would never know what polyimides might do for composites.

We explained the organization of our study, also its premises, and then we said we had prepared polyimide composite with the filament winding process, that we thought had about 5 v/o voids. It had an interlaminar shear strength of about 5,000 psi which was about 300% higher than anything observed to that date. We had anticipated that the shear strength would be higher at that void level, but then, our disappointment was moderated by the fact that the best boron-epoxy composites had shear strengths of only about 8,000 psi at that time. We had a few photomicrographs along to show void differences.

The response to the presentation was confusing to me. Most of the people, it seemed, did not want to belive anything I had to

say. The polymer people said that polyimides were extremely brittle, with very high moduli, not at all like epoxies. Others thought the voids did not matter all that much. I forget the many other things that were said, but, in general, I remember that the discussions were heated, the material presented struck most as being controversial at best and, at worst, in error.

I am convinced that the source of the difficulties I experienced at that meeting and the origin of the difficulties that most polyimide workers had at that time was a deep commitment to the idea that polyimides were uniquely different from other composite materials. Therefore, their attention was always focused on finding the differences between polyimides and other materials; and when apparent differences were observed, in a way, it was more satisfying than otherwise.

Now our processing approach did have a subtle difference from that of others. In order to make Skybond 703 process like an epoxy we had to treat the solvent as if it was not there during cure. We designed the process to discourage volatile matter from leaving the composite until postcure. We depended upon molecular diffusion of the volatile matter through the cured matrix, accompanied by volumetric shrinkage of the matrix, to achieve a dense composite, free of voids and volatile matter. I like to use the term "trapped volatile processing" to describe

the procedure. I do not believe that anybody else was trying purposely to "trap volatiles" in their composites at that time.

During the next year we refined our techniques, explored autoclave and compression molding with Skybond 703. We developed an autoclave process, achieved void contents below 3 v/o consistently with boron and graphite and shear strength over 13,000 psi at room temperature, about 10,000 psi at 500°F and 8,000 psi at 600°F. We assigned a maximum structural operating temperature of between 550 and 600°F to Skybond 703 since its strength begins to decline rapidly within this temperature range.

There were important negative features about this process which, I believe, are characteristic of all processes that involve classical polyimide resin, typified by the Skybond and Pyralin materials. These characteristics are extended cure times and postcure times, therefore long process span time; high shrinkage, therefore more difficult dimensional control, warpage and possible adverse effects from residual stress; precise prepreg controls over solvent retention and degree of polymerization, therefore more difficult quality control and precision in the preparation of prepreg and during its storage and its use.

Because of these adverse characteristics the economics of composites based on classical polyimides were not nearly as favorable as epoxies, if the objective was a high performance, high quality composite. However, therehas been a polyimide composite materials and processing technology available since 1968 which was applicable to many kinds of Aerospace structures.

In 1969 we had the opportunity to apply our previous efforts to some real structures under contract to Pratt & Whitney on AFML's Advanced Composite Engine Program. The application was to a jet engine fan blade operating at 550° F. Because of the modest size of this structure, because dimensional control was required on all molded sufaces, and because rather large quantities of blades might eventually be manufactured, matched-die compression molding was the natural molding process, the process of choice. We knew that we would be less troubled by the negative features of processing classical polyimides than if the application had been a large area that was natural for autoclave molding. We could work at lower solvent and higher staging levels in the blade application since there was much pressure and fast heating rates available to us. However, we had to work to tight dimensions and deal with complex layup orientation. We were very concerned about the possible effects of shrinkage and residual stress.

At about the same time period we began to hear about a new polyimide resin developed for NASA by TRW and called P13N. This resin was reputed to reduce much of the difficulty being experienced in processing other PI's. By that time I had come to classify composite resins not according to a chemical formula, but rather by considerations of processing and strength. I would organize resins into the following classes:

Class I: Tractability without solvent
Class II: Tractability with solvent
Class III: Tractability with solvent & volatile reaction products.

Sub-classes could also be constructed based on melting point (viscosity-temperature relationships), amount of solvent required for tractability, reaction temperature, etc. The classification system, therefore, was based on rheology and kinetics.

I could not tell from the literature into which class P13N belonged. It required much talking and prodding before we could come to the conclusion that P13N might really be treated as a Class I resin. As a Class I resin it did not require solvent for tractability and did not liberate volatile matter. In a couple of weeks in the laboratory we confirmed this approach and had observed a shear strength over 12,000 psi.

In order to process P13N as a Class I resin it is necessary, after impregnation, to apply a severe thermal treatment to it. During the thermal treatment solvent is eliminated and volatile reaction products are eliminated. What is left is a solid resin that requires over 500° F to melt (produce tractability) coupled with high viscosity and a high reactivity at or above its melt temperature. Matched-die molding handles these processing requirements very nicely. We substituted P13N for Skybond 703 early in the ACE Program and were glad of it.

We molded over 300 blades with boron and high modulus graphite fiber. We achieved shear strengths of 15,000 psi and void contents below 1 v/o routinely. The blades were severely fatigue-tested, thermally-cycled repeatedly and tested at 550° F, all sucessfully. The blades were less than half the weight of titanium. If not for the concern about the ability of composite fan blades to withstand large object impacts, I am convinced that P13N with graphite or boron would be driving the F-15 today.

If P13N is processed according to the methods appearing in the original publication, it became a Class III resin in our system of classification. Solvent is retained for tractability and volatile reaction products are liberated during cure. It quickly became similar to Skybond 703, subject to similar economics,

complexity and precision. There are quantitative differences in these factors just as there are between every Class III resin, but there are no differences in kind, in the nature of the problems they present. They are not nearly as attractive from my viewpoint as a Class I resin.

As best as I can recall, it was sometime in 1971 that I first began to hear about Gemon resin which reputed to be even easier to process than P13N although its thermal capability, in the range of 450° F, was somewhat less than what we had come to associate with polyimides. From the literature it was clear that Gemon was a Class I resin.

In 1972 we developed an interest in filament winding materials with higher temperature capability than epoxies. We procured some Gemon on glass roving and prepared NOL rings. At a very low volatile level, and with the use of heat to produce tractability, we prepared excellent composite from it. The shear strength at room temperature was equal to the best epoxies. At 500° F the shear strength was 8,000 psi, much better than the best epoxies.

Later we conducted a program for NASA/Lewis to evaluate Gemon/glass for metal-lined pressure vessels. We confirmed our earlier good experience with Gemon as a filament winding

resin. Pressure vessel performance was as good as epoxies at low temperatures with some useful strength at 600°F, but only for a very short time. Within the same NASA program we worked with a developmental variant of P13N, but had no success preparing a good wound composite with it. Its high melting point and viscosity after immidization precluded straightforward winding.

My most recent experience with polyimide composites was in 1973-74 on another AFML Program. As a sub-contractor to G.E. on the Advanced Composite Engine Static Structure Program, we fabricated a hot air fan bypass duct which operated at 450°F. It was a truncated cone, about 44 in. high, major diameter of 54 in. and minor diameter of 48 in., with Keramid 601/AS graphite skin bonded to HRP honeycomb with HT 424 adhesive. For 450°F operation that is a well-balanced combination of materials. Keramid was Gemon (essentially) but now available as a neat resin. We prepared the prepregs and conducted process and material characterization studies as well as fabrication of the duct.

We found early that the thermal stability of Keramid 601 was very sensitive to the solvent used for impregnation. Only n-methyl pyrollidone appears to allow this resin to achieve its best thermal performance. We found that the thermal stability

of Keramid 601 was actually better than we anticipated from our previous experience with Gemon, which was prepared with a different solvent. Not only did we observe shear values of over 17,000 psi, but also the ability to withstand heat aging at 500°F for hundreds of hours without apparent degradation. We have not had the opportunity to explore this material at temperatures in the 500 - 600 °F range since recognizing the solvent effect, and therefore we are not in a position to recommend Keramid 601 beyond a range of 450-500°F.

We found in our work that at a volatile content level of about 5 v/o, Keramid 601 with AS graphite could be processed as a Class I material. However, at this volatile level, the prepreg is dry, requiring heat for tack and contourability. This does add complexity to its processing and in-process quality control. Many fabricators are reluctant to work with these complexities, but it is the preimpregnator who has an even more difficult problem.

Dry resins do not lend themselves well to continuous pre-impregnation with unidirectional fibers. It is essentially impossible to make rolls with this type of material without gaps, variations in band width, etc. If the usual incoming material inspection that is applied to other graphite prepregs is applied to this sort of material, it is conceivable that the material

would never pass receiving inspection. At a volatile content level in the range of 15 v/o Keramid 601/graphite prepreg has all of the nice characteristics of good epoxy/graphite prepregs. Prepregers can handle this material well, and, naturally, prefer to prepare it this way. However, in this form, Keramid 601 becomes a Class II material and many of its advantages, from my viewpoint, have been sacrificed.

This is one of those situations in which the demands of the commercial preimpregnation process interferes with the compositing process. It is a perfect situation in which to introduce woven fabrics. This form of fibrous material does not depend upon the resin to bind the fibers together. Therefore, dry resin can be used, both by the preimpregnator and the fabricator, as has been done with glass fabric prepregs for many years.

I consider all of the polyimide resins that have been discussed to be state-of-the-art materials. They are all very different materials and a recommendation for the use of one or the other is very dependent upon the specific structure that is desired. For temperatures to 450°F probably to 500°F and possibly somewhat higher, Keramid 601 could be committed right now to large structures with relatively modest risk although substantially much more design and engineering data

than is now available would be required. The latter part of that statement is probably valid for all polyimide composites.

This, of course, is short of NASA's desire for a 600° F composite material. Although I have had little direct experience, the literature strongly suggests that NR150B is truly structural at 600° F and useful to possibly 700° F. The resin is described as a thermoplastic with a high glass transition temperature. The literature description of its processing indicates that it had been treated as both a Class I and Class II resin. The lower pressure autoclave techniques appear to be Class III processing, wherein these appear to be an attempt to provide a delicate balance between pressure, solvent removal, polymerization and heating rates. There is not yet sufficent data to clarify the reliability and reproducibility of the methodology to large and complicated composite structure. The technique of pressurizing and forming fully-reacted, volatile-free composite at very high temperature is Class I processing and should be practical for certain shapes. NR150B is a unique resin. It should receive serious consideration by NASA.

Another type of material that is beginning to receive attention is bis-maleimide resin. The thermal performance appears to be similar to Keramid 601, but it may offer the advantage of greater liquidity at lower temperature. This could reduce the

problems of preimpregnation, tack, etc. that I have described for Keramid 601.

DuPONT RESPONSE

STATE-OF-THE-ART

NR-150 POLYIMIDE SOLUTIONS

Section A Polyimide Matrix and Adhesive Resins

A-1-a Designation and Source - The Plastics Department of Du Pont is the sole producer and supplier of NR-150 polyimide binder and adhesive solutions.

A-1-b Type - NR-150 polyimide binder solutions undergo condensation polymerization to yield high molecular weight, amorphous, non-crosslinked thermoplastic resin. Two different resin systems are offered which produce polyimides having different softening temperatures (glass transition temperature or Tg). NR-150A2 has a Tg of 550-572°F and NR-150B2 has a Tg of 662-700°F. Mixtures of A2 and B2 having Tg's intermediate between A2 and B2 are also available.

A-1-c Form - NR-150 products are sold as solutions in N-methylpyrrolidone. The binder solutions are high solids (45 wt. %), low viscosity (50-130 poises) solutions suitable for prepregging. The adhesive solutions are higher viscosity (2000 poises), lower solids (35 wt. %) suitable for application by brush or roller coating.

A-2-a Maximum Use Temperature (Air) - The time to 50% retention of the flexural strength of graphite fiber composites is estimated to be about 50,000 hours at 500°F, 4,000 hours at 600°F, and 500 hours at 700°F.

A-2-b Environmental Effects

Moisture: The mechanical properties of NR-150 are not seriously affected by prolonged exposure to boiling water. The equilibrium water absorption at 50% R. H. is about 1 weight %.

Fuels: NR-150 neither absorbs nor is stress-cracked by either aviation or automotive fuels.

Vacuum: NR-150 has been shown to undergo very low vacuum outgassing.

Radiation: NR-150 has been shown to be very resistant to high energy radiation.

Flammability - Oxygen Index = 60

Flammability Rating = 94V-0.

A-2-c Possible Health Hazards - The solutions contain products of aromatic dianhydrides and aromatic diamines dissolved in N-methylpyrrolidone which may be harmful is absorbed through the skin and which may cause irritation if contacted with the eyes. Precautions should be taken to avoid such exposure as well as inhalation of the vapors. Tests to date indicate

that the aromatic compounds do not appear to have carcinogenic activity.

A-2-d Processing Limitations

Producing Resin - No limitations

Manufacturing Prepreg - No limitations

Lay-Up and Cure of Structural Components - Best results are obtained with vacuum bag/autoclave processing. High temperature autoclaves or heated tooling will probably be required. Processing temperatures are usually 50-100°F above the resin softening temperatures. The processing temperature for the NR-150A2 system is usually 600-650°F and for NR-150B2 is usually 750-800°F.

A-2-e Compatibility with Graphite Fibers - NR-150 binders have been shown to adhere well to all types of graphite fibers.

A-3 Experimental NR-150 Compositions Predicted to be Commercially Available within 5 Years - Du Pont has an ongoing research and development program on NR-150.

Section B Availability of PI Resins

B-1 Raw Materials - All of the NR-150 precursor materials are produced within Du Pont and can be manufactured in the volumes projected for the future. The solvent, NMP, is commercially available from GAF-Inc.

B-2 Impact of Government Regulations - There are no special OSHA or EPA regulations governing the use of NR-150 polyimide solutions or any of its components and none is anticipated.

B-3 Influence of Non-Aerospace Markets on the Quality and Quantity of Resins Available - The use of NR-150 in non-aerospace markets will help to establish a broad non-cyclical base. The development of such markets will not adversely affect product quality. The resin production will be sufficient to meet market demands.

B-4 Effect of the Changing Economic State of the Du Pont Company - Provided that the demand for NR-150 continues to grow, its production should be relatively immune to the changing economic state of the Du Pont Company. The monomers and the solutions can be made in existing facilities within Du Pont.

B-5 Future Availability - It is the inte of Du Pont to continue to offer for sale NR-150 polyimide solutions as long as steady growth continues and significant markets develop. Considerable growth is expected over the next 20 years.

Section C Manufacturing Processes and Equipment

C-1-a . Processes for Producing Resins - The processes for producing NR-150 solutions have been well defined

and the systems are now being produced on a routine basis.

C-1-b Processes for the Manufacture of Prepreg Tape - The facilities of the Du Pont plant at Saugus, California can be used to prepare prepreg tape. Prepreg tape has been successfully prepared by at least two other commercial prepreggers.

C-1-c Specifications for Resins - NR-150 polyimide solutions are specified with respect to solids content, solution viscosity, density, and Tg of the fully cured resin.

C-1-d Quality Control and Non-Destructive Evaluation Methods - Each individual batch of NR-150 binder solution is checked for solution viscosity and solids content. Monomer purity is also rigidly controlled.

C-2-a Equipment for Resin Manufacture - NR-150 polyimide solutions are prepared in facilities already in existance in Du Pont. Prepreg tape can readily be prepared by commercial prepreggers, including the Du Pont Saugus, California plant.

C-2-b Equipment for Non-Destructive Evaluation and Quality Control of Large Structural Components - Du Pont has no plans to manufacture large structural components.

C-3-a Major Problems Associated with Establishing Adequate Manufacturing Specifications - To date, the manufacturing specifications already established have been adequate. Other specifications can be added if necessary.

C-3-b Major Problems Associated with Fabricating Large Structural Components - There has been no experience in fabricating large structural NR-150 components to date. No major problems are anticipated.

Section D Preprietary Nature of PI Resins

D-1 Preprietary Nature of NR-150 - Limitations in Establishing Adequate Specifications for Quality Control - Since the NR-150 monomers, as well as the binder solutions, are made within Du Pont, there should be unusually good quality control.

D-2 Proprietary Nature of NR-150 - Influence in Long term Availability - As Du Pont manufactures the monomers used for NR-150 polyimide systems and the intermediates for the monomers. No problems are anticipated with the availability of NR-150 systems in the future.

Section E Limitations of PI Resins

E-1 Maximum Potential Use Temperature - NR-150 polyimides should not be used above the softening temperature of the resin when under mechanical stress,

otherwise creep will occur.

E-2 Long Term Durability - see Section A-2-a - Du Pont considers NR-150 to be the most stable of all polyimides.

E-3 Degree of Difficulty in Manufacturing Large Complex Shapes - Large complex structures can be molded using vacuum bag/autoclave equipment. Either the entire autoclave can be heated or heated tooling can be employed with the autoclave being used as a pressure vessel. Thick composite sections (over 1/2 inch in thickness) which have low void levels can be readily molded in one operation. Because of the thermoplastic nature of NR-150 polyimides matched die molding of large flat laminates followed by a post forming operation appears to have great potential.

Section F New Resin Systems

F-1 Potential Replacements or Competitors for NR-150 - No other high temperature resin system competes directly with NR-150. NR-150 is unique in that it offers processing versatility (vacuum bag/autoclave and compression molding as well as thermoformability), the ability to produce low void laminates in an all aromatic polyimide, unusual matrix toughness, excellent high temperature strength retention, superior long term thermal-oxidative stability, application versatility

(can be used as a binder and adhesive, chopped fiber molding resin and a coating resin) - all at a reasonable price.

G-1-b Price - Resins - The monomers used for NR-150 systems are produced by Du Pont. Because of the fluorine containing groups in the dianhydride monomer, NR-150 systems will always be higher priced than concentrated thermosetting aromatic polyimide materials.

G-2 Major Factors which will Influence Changes in Costs - The major factor influencing the price of NR-150 polyimides is the sales volume. The price of NR-150 will decrease as the sales volume increases.

SUMMARY

The advent of NR-150 polyimide binder and adhesive solutions represents a significant advance in the state-of-the-art. Thermally induced condensation polymerization yields a linear, high molecular weight, amorphous thermoplastic polyimide. Voids produced by volatiles evolution can be readily eliminated by pressuring above the Tg. Because high Tg's are attainable, excellent mechanical property retention can be realized in the 500-700°F temperature range. The combination of low voids and an intrinsically stable aromatic polyimide chain results in extraordinary thermal-oxidative stability. Lack of crosslinking means that the NR-150 matrix is unusually tough resulting in improved resistance to temperature cycling, fatigue, and impact. No limitations are foreseen in the fabrication of large complex shapes. Indeed, NR-150 composites possess great processing versatility. Not only can parts be vacuum bag/autoclave and compression molded, they can also be thermoformed. Thick cross-ply laminates, free of voids and cracks, can be molded in one operation. There are no unusual health hazards involved in handling the binder solutions. In short, NR-150 binders and adhesives should be ideal for use by NASA in the space shuttle.

GENERAL DYNAMICS RESPONSE



GRAPHITE/POLYIMIDE COMPOSITES

W. G. SCHECK
GENERAL DYNAMICS CONVAIR

General Dynamics, Convair Division has had extensive experience in the handling and processing of quartz/polyimide composites. Nearly 3000 quartz/polyimide radomes have been manufactured in the past four years. This experience has allowed Convair to proceed at a rapid pace into graphite/polyimide composite studies. Convair is a purchaser of polyimide prepreg and adhesives and conducts no basic resin development. Efforts are directed at developing usable processing techniques. Thus, the following review of the state-of-the-art of graphite/polyimide composites is from a user's viewpoint, not a developer of materials.

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GRAPHITE/POLYIMIDE COMPOSITES

W. G. SCHECK
GENERAL DYNAMICS CONVAIR

A. POLYIMIDE (PI) MATRIX AND ADHESIVE SYSTEMS

1. Several different polyimide resin systems have been on the commercial market for the past 10 to 15 years. The earliest polyimides were the condensation type, followed by the addition, and recently by the thermoplastic resins. In Table 1 a listing of these resins as to type, form, resin producer, and prepreg supplier is shown. The systems shown are the ones that have been either fully characterized or at least have been partially characterized by industry. In Table 1 the Monsanto 703 resin has been modified by both Brunswick and Whittaker R&D and has a different number, but is not shown separately. Also, the NR150 resin manufactured by DuPont is a series of resin systems and has not been broken out into separate categories. Only two commercially available polyimide adhesive systems have been characterized and they are the FM-34 and Hexcel 901 which are based on condensation type polyimide resin systems.

2. The maximum use temperatures for each of the resin systems for short, intermediate, and long term exposures are also shown in Table 1. These temperatures were selected on the basis of full atmospheric pressure and could

TABLE 1
POLYIMIDE RESINS

Resin	Type	Resin Supplier & Form	Prepreg Source	Maximum Temperature °F		
				Short	Medium	Long
700	C	Monsanto-L	DuPont	600	550	500
703	C	Monsanto-L	WRD	800	550	550
709	C	Monsanto-L	USP	600	550	500
710	C	Monsanto-L	USP	800	650	600
4707	C	DuPont-L	USP	600	550	500
P13N	A	Ciba Geigy-L	DuPont	600	500	500
P10P	A	Ciba Geigy-L	WRD	600	500	500
P105A	A	-- -L	--	600	500	500
K601	A	Kerimid-L	DuPont	450	450	400
K603	A	Kerimid-L	DuPont	450	450	400
HX-580	A	Hexcel-F	Narmco	600	500	500
H4397	A	Hercules-F	Hercules	500	500	450
NR150	TP	DuPont-L	DuPont	600	600	600
2080	TP	UpJohn-L	DuPont	550	550	550

all be increased if the pressure (oxygen content) was decreased. The hydrolytic stability of the condensation polyimides is excellent (85% of high temperature properties after exposure to humidity), the addition polyimides have moderate resistance, and data obtained to date by Convair on thermoplastic polyimide resins has shown excellent resistance to humidity. Fuels, vacuum, and radiation have little effect on polyimide resins; however, paint stripper does effect and can eventually completely destroy a polyimide laminate. No known possible health hazards exist with the exception of the P105A resin which has been recently removed from the market because of OSHA requirements.

The Monsanto 710 polyimide resin is the only condensation resin that seems to have a significant variability from batch to batch of resin. Convair's prepreg material suppliers have not indicated any major difficulties with any of the systems other than 710. The material suppliers report that the addition and thermoplastic systems appear to be easier to handle than the condensation polyimides.

In laying up the prepreg, the condensation systems require a precompaction step, the addition polyimides require slight heating to obtain tack and drape, and the thermoplastics require no special techniques. In fabricating

structural components, the condensation systems are the most difficult, because of the evolution of volatiles, and both the addition and thermoplastic polyimide systems can be handled much like epoxies except for the higher cure and postcure temperatures required.

All of the polyimide resins have been found by Convair to be compatible with the commercially available graphite fibers. However, Type A-S or Thornel 300 should not be exposed for extended times at temperatures above 500°F.

3. Most of the commercial resin activity has been aimed at developing new resin systems for the 400 - 500°F temperature range. Two new potential systems are the Kerimid 353 and the Hercules 4397 addition resins. The PMR polyimide resin developed at NASA-Lewis shows excellent 600°F properties, but it is doubtful that it can be used for large structures because of the problems involved in manufacturing the prepreg.

B. AVAILABILITY OF PI RESINS

There seems to be no significant problem in availability of raw materials other than those associated with any resin system because of the recent energy shortage. Non-aerospace markets require development, otherwise, the evolution of polyimide resins in availability, reliability, and cost will remain in the same state as they are today. The avail-

C-2

ability and cost of polyimide resins depend solely on finding a commercial application for these systems. If there is not a commercial application found in the next ten years, only a very few high priced resin systems will probably be available.

C. MANUFACTURING PROCESSES AND EQUIPMENT

1. Convair does not produce resins or adhesives, but rather purchases prepreg or adhesive systems to Convair specifications. The materials are procured on the basis of these specifications to meet certain mechanical and physical properties in both the uncured and cured conditions. Convair currently has material and process specifications for the Monsanto 703 and 710 resin systems on a number of graphite, glass, and quartz reinforcements. A new specification for the HX-580 (F-178) addition resin is currently being written. Convair's quality control and nondestructive evaluation methods include determining the resin content, volatile content, and flow of the prepreg; C-scan of the laminates; and resin content, fiber content and specific gravity of the cured laminates.

2. Convair has autoclaves that have the capability of going to 800°F and 200 psi pressure. However, the size limitation of any component to be manufactured which requires a cure temperature above 400°F and pressure beyond normal

vacuum bag pressure is five feet by four feet. Convair has adequate C-scan equipment and uses tag end specimens to ensure the quality of the fabricated parts.

3. The two major problem areas in fabricating large structural components is the evolution of volatiles during cure and the requirements for higher temperature presses and autoclaves than are readily available throughout industry.

D. PROPRIETARY NATURE OF PI RESINS

All of the current available polyimide resins are proprietary. Convair has developed resin specifications as well as material and process specifications. The material and process specification is the prime control item at Convair and will continue to be so in the future. Until there is a major application in the commercial area, specifications will not have any influence on the long term availability, except that manufacturers of the resins will quit making the resin for lack of a market.

E. LIMITATION ON PI RESINS

All of these factors have been discussed in other sections of this document.

F. NEW RESIN SYSTEMS

1. Other candidate resin systems which could potentially replace the polyimide resin systems include PQ, PPQ, or PIQ. All of these systems are very expensive and require

very high temperature presses and autoclaves. The resin development work has been primarily funded by NASA-LeRC and AFML on a low level because there have not been any specific applications. At the current time the only known material supplier is Whittaker R&D. Some of the solvents currently used, primarily creosol,could cause major health problems.

G. PRICE

1. The polyimide resins vary from slightly higher than epoxies to very expensive like NR150. The graphite/polyimide prepreg is generally $100 to $175 per pound. The HX-580 prepreg is exceptionally high at $275 per pound. The PPQ prepreg costs about $400 to $500 per pound. All of these prices are for less than 100 pound quantities. If the total poundage of polyimide prepreg would increase substantially, material suppliers such as Hercules have stated the material would only be slightly higher than graphite/epoxy prepreg. If the condensation polyimides are used, the cost of graphite/polyimide composites will be higher than graphite/epoxy composites because of increased bleeder, vacuum lines, and potential failures during the cure cycle. The addition and thermoplastic polyimide resin systems should not be any more costly than epoxy systems.

MCDONNELL DOUGLAS RESPONSE

MCDONNELL AIRCRAFT (MCAIR) POLYIMIDE COMPOSITES

MCAIR's experience has been primarily with Monsanto's Skybond 703 condensation reaction polyimide resin reinforced with boron and Modmor II graphite fibers. These material systems were used to fabricate a polyimide composite F-4 rudder that successfully passed all structural tests. Structural testing of an F-15 wing compression panel with these same materials was less successful. In addition to the Skybond 703 matrix composites, we have also done limited laboratory testing of several addition reaction/thermoplastic polyimide resin based composites.

A. Polyimide Matrix and Adhesive Resins

1. Commercially available resins:

   a. Monsanto Skybond series of condensation reaction laminating resins with thermal stabilities of 550 to 650+°F. Skybond 703 and 710 have been most widely used in boron and graphite reinforced laminates.

   b. DuPont Pyralin 4701 and 4707 condensation reaction laminating resins with thermal stability of 600 to 700°F. DuPont NR150 series of thermoplastic polyimide laminating resins are potentially useful to 500 to 650°F depending on which NR 150 resin is used.

   c. Ciba-Geigy P105A addition reaction laminating resin and adhesive resin system. This resin may have been dropped from the market - temporarily or permanently. This resin is useful to 500 to 575°F.

d. Rhodia Kerimid 601 laminating/adhesive addition reaction polyimide resins. This resin is useful to about 500°F.

e. Bloomingdale FM 34 supported film adhesive and FM 29 core splice foam adhesive. Condensation reaction polyimides.

f. Narmco 840 supported film polyimide adhesive (condensation reaction type).

MCAIR has had experience with all the above resins in combination with boron or graphite fibers except Monsanto Skybond 710 and DuPont Pyralin 4701. Our most extensive experience has been with the Skybond 703.

2. Significant Characteristics

a. Temperature use limits for condensation reaction polyimides range from 550 to 650+°F. Our experience with Skybond 703, Bloomingdale FM 34 and FM 29, and Narmco 840 indicated excellent thermal stability for 100 to 500 hours at 550°F. Long term tests were not performed above 550°F. Long term temperature exposures have not been run by MCAIR on any addition reaction polyimides.

b. MCAIR has not conducted any environmental exposure tests on cured laminates. However, we have observed the detrimental effect of atmospheric moisture on condensation reaction polyimide prepreg, particularly boron/Skybond 703.

c. Processing limitations for laying up and curing condensation reaction polyimides revolve around

(a) getting much of the volatiles out of the prepreg so that a good quality laminate can be fabricated, and (b) once the volatiles are driven out the prepreg becomes very difficult to handle for part fabrication. Our more limited experience with addition reaction polyimides indicate some of the same type of problems. Cure cycles for condensation reaction polyimides are satisfactory (350F/100-200 psi), but post cure schedules are very long. We ran post cure schedules up to 120 hours. If the volatile content was kept high, the prepreg drapability, tack, handleability was much improved - but, curing good quality laminates consistently could not be attained.

d. MCAIR tests have been conducted with Modmor II graphite fibers on condensation reaction polyimides, and Hercules AS or Union Carbide T300 on the addition reaction polyimides.

C. Manufacturing Processes and Equipment

1. Specifications/Quality Control - We have written both material specifications and prosess specifications for fabricating polyimide based aircraft type structure - F-4 rudder and a small F-15 wing compression panel. These articles were also nondestructively tested with standard techniques. The real crux of specifications/quality control problems is controlling the prepreg prior to cure since repeatability has not been significantly demonstrated. The "A" and/or "B" staged resin must be knowingly controlled from base resin supplier through

prepreg manufacture operations. Only when this control is maintained can uniformly acceptable polyimide laminates be fabricated. Initial efforts in this direction by MCAIR have identified some of the variables needing control for condensation type polyimides, however this work may only have scratched the surface of what will eventually be required. We have written specifications for fabricating laminates and performing NDT operations on these laminates. NDT was satisfactory for detection of various flaws.

2. Equipment - Structural component fabrication from condensation/addition reaction polyimide prepreg requires autoclaves capable of 350F and 100 to 200 psi pressure. In addition, a suitable vacuum pumping system (with cold traps) and numerous vacuum ports must be included on the tool so that easy volatile removal is guaranteed. Thermoplastic polyimides (DuPont NR150) require 575 to 700°F "cure" under 100+ psi pressure autoclave cycles. Steel tools would be most desirable because post curing to approx. 600°F should be done on the tool to guarantee conformance to contour requirements. Steel is more stable than other candidate tool materials. Currently available radiography (in-motion) and "C" scan equipment is suitable for polyimide part/structure NDT evaluation. NDT requirements would probably be no different than current requirements for epoxy matrix composites.

3. Major Problems - Manufacturing specification/large structural component fabrication problems center around four (4) principal problems:

a. Determining that the current batch of polyimide prepreg is identical in processing characteristics to the batch(s) on which the specification is based. There has not been a true production environment for polyimide composite prepregs.

b. Handling/drapability qualities of highly "B" staged, non-tacky polyimide prepreg. This is especially a problem for contoured, substructure type parts.

c. Ability to fabricate thick parts - 1/8" or thicker - has not been reliably demonstrated and must be suspect, especially for the condensation reaction polyimides. Large area, thick parts have not been fabricated successfully.

d. Long post cure times (several days) for condensation reaction polyimides. Ties up shop equipment for excessive periods of time.

D. Proprietary Nature of Polyimides

The proprietary nature of polyimide resins is no different than the proprietary nature of the current, widely used epoxy matrix composite prepregs and adhesives. Resin suppliers are extremely reluctant to divulge any proprietary formulations outside their companies. There has not been a production environment for polyimide composite prepregs that could demonstrate whether proper batch-to-batch

control is being exercised by the resin manufacturer and prepregger. The key issue is whether the supplier can demonstrate that sufficient tests and checks are performed to guarantee resin batch consistency. If the resin formulation is not divulged, we would attempt to analytically identify the resin constituents and establish control values based on mechanical/physical property performance.

E. PI Resin Limitation

1. Temperature Limits - Condensation reaction polyimides have tempeature limits between 550F and 650+°F, depending on use conditions. We have exposed polyimide laminates to 100 hours at 550F exposure and adhesives to 500 hours at 550°F with excellent property retention. Data in AFML TR 72-91. Addition reaction polyimides have temperature limits somewhat lower (450-575°F) depending on application. We have short term data only at 550F and 600F.

2. Long term durability is an unknown factor. Laboratory type data from government funded programs indicate that polyimide resins are more environmentally resistant, especially from moisture, than are epoxy resins. However, long term durability also infers maintainability and repairability. Field repairing of polyimide composite primary structure has never been investigated to our knowledge. This could be a very difficult problem - field repairing with materials requiring extensive cure cycle time and high cure pressures.

3. Manufacturing difficulty for large, complex shaped structures consists of:

a. Prepreg handleability particularly lack of tack, for condensation reaction polyimides.

b. Volatile removal from entire part during cure, particularly from the part center of large area components.

c. Predictability of prepreg resin uniformity over entire part. Batch-to-batch consistency not yet demonstrated and exact controls needed are not yet generally known.

d. Lack of cured resin "toughness" for both laminates and adhesives. Low peel strength, etc. could influence bonded joint performance, edge machining or fastener hole drilling.

G. Price

Graphite/polyimide prepreg prices to MCAIR have only been based on R&D quantities, and, therefore, do not reflect true market potential cost. R&D prices for G/PI in 1971-1972 were approximately $200/lb. It is very difficult to assess the actual G/PI prepreg price for volume production since only R&D quantities have ever been produced.

SUMMARY

MCAIR feels that polyimide composites require extensive development effort before any committment could be made for production of primary structural hardware. Our experience has been primarily with condensation reaction polyimides with which we have fabricated an F-4 rudder and an F-15 wing compression panel. The rudder was successfully tested while the wing panel was less successful. Major development areas required for polyimide matrix composites are:

a. Polyimide prepreg resin consistency must be improved so that material and process specifications could be established with the same confidence level as epoxy matrix composite specifications.

b. Manufacturing techniques must be developed for better prepreg handleability, large surface area and thick part fabrication, highly contoured part fabrication, and reduced cost.

c. Mechanical property data must be generated to establish design allowables, strain limitations, fatigue characteristics, K_t effects of fastener holes, hybrid potential, and peel/toughness characteristics.

d. Prepreg resins and adhesives must be developed at the same speed so that a bonded structure capability is established.

Effort in these areas has dropped off in the last several years primarily because of the lack of extensive hotter (400+°F) near term military airframe applications. This trend has concentrated

more effort on epoxy matrix composites rather than the high temperature systems such as graphite/polyimide.

MONSANTO RESPONSE

MONSANTO RESPONSE

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GRAPHITE-POLYIMIDE COMPOSITE MATERIALS

SUMMARY

Monsanto Company is a major supplier of basic polyimide precursor resin solutions sold under the trademark Skybond® for matrix and adhesive use. It does not sell prepreg products or finished parts. The Skybonds are of the condensation type and offer the highest thermal-oxidative stability of any commercial resin. Long life at 600°F. in air has been demonstrated with short-term utility shown at 800°F. and useful ablative properties under very high heat flux conditions. The non-flammability properties in air and the essentially smokeless degradation of Skybond resins in a flame environment make these products of special interest. They are made from commercially available raw materials in non-specialized equipment and can be provided in quantity upon short notice. In-house research has concentrated upon glass cloth composites but fabricators have made structures with boron and graphite fibers. Polyimide resins of even greater stability have been prepared experimentally.

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GRAPHITE-POLYIMIDE COMPOSITE MATERIALS

INDUSTRY ASSESSMENT

—

REPLY TO NASA QUESTIONNAIRE

BY

MONSANTO COMPANY

FEBRUARY 27, 1975

GRAPHITE-POLYIMIDE COMPOSITE MATERIALS

Reply to Questionnaire

A. Polyimide Matrix and Adhesive Resins

1. The following polyimide resins are commercially available from Monsanto. All are of the condensation type.

Designation	Form
Skybond® Resin 700	Solution
Skybond Resin 703	"
Skybond Resin 705	"
Skybond Resin 709	"

In addition, specialty products which include Skybond Resin 710, foam precursor powder RI-7271, and others, are offered.

2. Significant Characteristics

   a. The maximum use temperatures for these resins, based upon 12-ply E-glass laminate aging studies in air, are estimated below. (Obviously, strength levels with graphite would be much greater.)

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	Time to 20,000 psi end point	Aging Temp. °F.
Very short-term exposure	10 hours	800
Short-term exposure	100 "	700
Intermediate-term exposure	1,000 "	600
Long-term exposure	10,000 "	550

b. The cured resins have excellent resistance to moisture if alkaline conditions are avoided. They are unaffected by JP-4 fuel and Skydrol functional fluid. Good adhesion and very low out-gassing have been reported in a vacuum environment, and radiation resistance is high. Acceleration of degradation in the presence of light, air and moisture has been reported.

c. Possible health hazards in working with polyimide resins include those to be expected from traces of aromatic amines and aromatic anhydrides, solvent vapors, and traces of unknown volatile products produced during cure and post-cure. Good ventilation and minimal skin contact is recommended, although no health problems have been brought to our attention. Toxicological tests have

determined the oral LD_{50} value (rats) for Skybond Resin 700 to be 6950 mg/kg.

d. Processing variables for resin production are readily controlled. Preparation of prepreg requires control of volatiles and cure advancement dependent upon the laminating and cure conditions established by the specific fabricator. Void contents of less than 1.5% have been measured on graphite/Skybond Resin 703 composites.

e. Compatibility with graphite fibers has been demonstrated by the preparation of complex high strength composites from Skybond Resin 710 by aerospace fabricators.

3. An experimental polyimide varnish which cures to the most oxidative-thermally stable polyimide known has been prepared in the laboratory from commercially available raw materials. Commercialization will be dependent upon properties of composites and market factors.

B. Availability of Polyimide Resins

1. Adequate sources exist for all Skybond raw materials well beyond anticipated levels of use.

2. The products are manufactured without air or water pollution, and it is believed that prepregging and lamination processes can be similarly controlled. Consequently, compliance with emission and effluent regulations represents no problem.

3. At present, non-aerospace markets for polyimide matrix resins are relatively small and are not likely to affect the overall quantity and quality of available resins in the foreseeable future. Significantly lower raw material costs would likely accelerate the development of larger volume applications.

4. The changing state of the economy will not alter the availability of Skybond Resins to the aerospace industry.

5. The polyimide product line may change with the development of new and improved resins, as with any product group. However, manufacture of any of the currently available Skybond Resins will continue if needed by NASA.

C. Manufacturing Processes and Equipment

1. The processes for producing Skybond Resins are well defined and the resins have been supplied

routinely for a number of years. Scale-up to larger volume equipment has been readily achieved as required.

Resins specifications include viscosity, solids and sp. gr. with appropriate quality control tests to measure these properties.

2. The equipment to manufacture our polyimide resins consists of standard polymer production units which enable supply in drum or bulk quantities.

3. Skybond Resins have exhibited a high degree of reproducibility and with close control of conditions and substrate, good composite reproducibility is attained. The importance of substrate history and nature of the surface cannot be overemphasized. Both can greatly affect the properties of the prepreg and the composite. The fabrication of large structural components required by fabricators has been accomplished by careful attention to layup construction and time/temperature/pressure cycles.

D. Proprietary Nature of Polyimide Resins

1. The exact composition of all of the components making up Skybond polyimide resins has not been

disclosed. However, the general chemical nature of the products are known and specifications, which define resin content and which relate to shelf life of the products, have provided satisfactory quality control.

2. The proprietary nature of the resins is not expected to limit their long-term availability.

E. Limitation on Polyimide Resins

1. Maximum potential use temperature depends upon time, the environment and the application. With the development of more thermally stable polyimide resin systems, the use temperature may be expected to increase beyond 600°F. for 1000 hrs. continuous exposure in air.

2. The durability of composites can be expected to be very high, except under alkaline conditions, because of the chemical and solvent stability inherent in the polyimide structure. Again, the environment will determine the life time to be expected but at least 10,000 hrs. at 550°F. has been indicated with E-glass laminates.

3. Although Monsanto has not been directly involved in the manufacture of complex structures, our customers have indicated that carefully con-

trolled procedures must be followed in both prepreg and laminate manufacture to obtain structural uniformity. Large parts have been successfully made routinely - so it can be done. As experience is attained, the values of key parameters involved can be better predicted for specific part sizes and shapes.

4. The cost of polyimide resins has limited their market growth. Although cost has probably had little influence on the development of specialized aerospace applications, it has restricted expansion into other market areas.

A performance limitation has been referred to above - that of degradation under basic conditions. A further constraint is the lack of flexibility of the cured resin, which, while contributing to high modulus composites, might be undesirable in certain other applications.

F. New Resin Systems

1. A variety of resins which do not contain the imide structure have appeared on the high temperature scene in recent years. Among these are the following types:

Polyphenylene sulfide

Poly(p-oxybenzoyl)

Polyethersulfone

Poly(p-benzamide)

Polymeric chelates

Friedel-Crafts polymers

Poly(benzimidazoles)

Phosphate-phenolic resins

Poly(phenylene)

Poly(quinoxaline)

Ladder polymers

2. The first four of the above offer thermoplasticity which can be utilized in injection molding operations. Limitations in strength at high temperatures and long term oxidative stability may be expected compared to polyimides. In certain applications, they may perform adequately and offer lower processing costs.

The latter members of the list offer high temperature rigidity and in general require in situ cure. Problems of processibility, toxicity, and the unavailability and expense of starting materials have been indicated. At the present time, these newer materials do not appear to

threaten imide-containing polymers as the premium high temperature resin type.

3. It is unlikely that the above would have any impact on the availability of Skybond polyimides.

G. Price

1. Current key raw materials for Skybond products range from ca. 60¢/lb. for solvents such as N-methylpyrrolidone, to ca. $3.00/lb. for a dianhydride such as BTDA. Based upon recent economic trends, these raw material prices may rise further due to inflationary pressures and oil availability. Significant increases in use, in resins other than polyimides and in areas other than aerospace, are conceivable and would help reverse this trend.

Resin costs are of course closely related to raw material costs and to conversion expenses, and polyimide prices would reflect changes in both categories. Skybond Resins must still be classified as specialty products and are produced in modest volumes compared to most of our commercial materials. They are volume-sensitive and a significant increase in usage, say a ten-

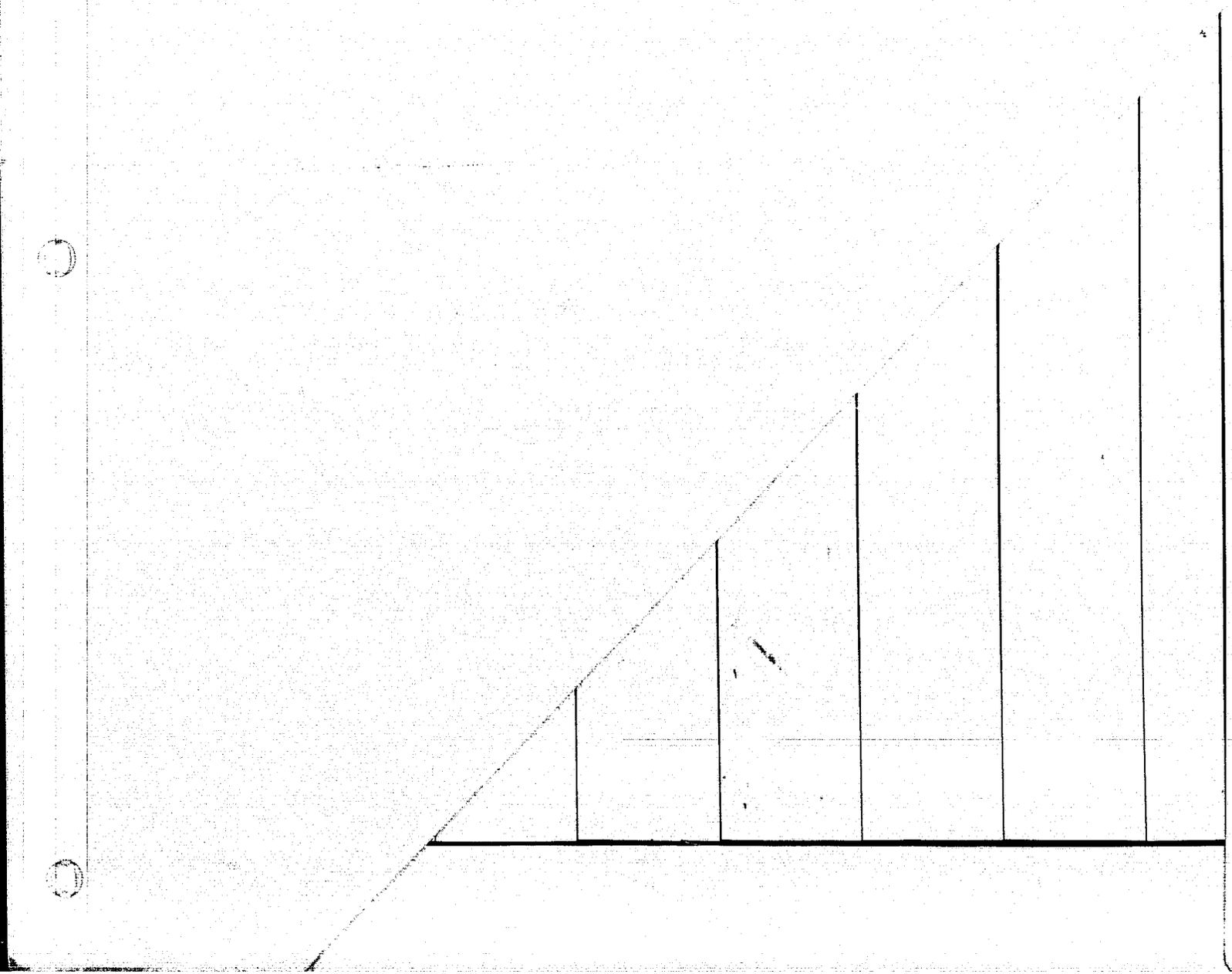
fold growth, would result in lower production costs and hence prices lower than the current $5.65/lb. of reactive solids for Skybond Resin 700.

2. Thus, the major factors which will influence changes in costs are (1) raw material prices, which ultimately are dependent upon (2) petroleum availability and (3) petroleum price, and (4) conversion costs which are dependent largely upon (5) labor and, (6) production volume and (7) energy costs.

Submitted by:

Albert H. Markhart
Monsanto Company
February 27, 1975

ROCKWELL INTERNATIONAL RESPONSE



DETERMINATION OF THE STATE-OF-THE-ART FOR GRAPHITE-POLYIMIDE COMPOSITE MATERIALS

By

S. Y. Yoshino

Rockwell International

Space Division

Downey, California

A. POLYIMIDE MATRIX AND ADHESIVE RESINS

1. Commercially Available Resins:

a. Designation and Source

1. Skybond Series	-	Monsanto Corp.
2. Pyralin Series	-	Dupont Corp.
3. Kerimid Series	-	Rhodia Corp.
4. HX-580 or F-178	-	Hexcel Corp.
5. Polyimide 2080	-	Upjohn Corp.
6. P-105A	-	Ciba-Geigy
7. P-13N	-	TRW Systems
8. HR-600	-	Hughes Corp.*
9. PMR Polyimides	-	NASA/Lewis*

*Not available commercially

b. Type of Polyimide

Monsanto and Dupont are producers of condensation-type

polyimides. Dupont also produces a "modified" addition type and a thermoplastic condensation type, NR-150. All of the other producers make addition types of polyimides.

c. Forms of Polyimides

Rhodia Corp. produces liquid, powder, and film forms of polyimide. Hexcel produces liquid and film forms of polyimide. The remaining polyimide producers make liquid forms of polyimide.

2. Significant Characteristics:

a. Maximum Use Temperature

Most polyimide systems are limited to intermediate exposure times of 1,000 hours or less. Rhodia Corp. and Hexcel Corp. addition type polyimides are limited to 500°F exposure. Other producers of condensation type polyimide resins claim 550°-700°F exposure stability.

b. Environmental Effects of Moisture, Fuels, Vacuum and Radiation

The moisture resistance of polyimides is superior to the epoxies. They also exhibit resistance to degradation by most solvents and fuels. Strong alkalis, however, degrade polyimide material. The polyimides also display low outgassing characteristics in hard vacuum.

One source of information also stated that they show good resistance to nuclear radiation and have low or non-flammable properties even in enriched oxygen atmosphere.

c. Health Hazards

No unusual health hazards are associated with the polyimide solutions utilizing n-methyl pyrrolidone, used by all but a few resin suppliers. A few suppliers do use DMF (di-methyl formamide) which is under investigation by OSHA as a possible carcinogen.

d. Processing Limitations

1. No processing limitations associated with production of the resin or prepreg.
2. Curing of structural parts utilizing certain polyimide resin systems such as Hughes' HR-600, Dupont's NR-150, and Ciba-Geigy's P-13N require very high pressures and temperatures to attain acceptable composite and resin properties.

   The addition types exhibit relatively good drape and tack characteristics - the condensation types are generally stiff and boardy with little or no tack, causing some layup problem on more severely compound-contoured assemblies.

e. Compatibility with Graphite Fibers

No compatibility problems, good shear strengths.

3. Experimental P.I.-Commercially Available Next 5 Years:

a. Hughes HR-600

b. PMR polyimides

c. NR-150

B. AVAILABILITY OF P.I. RESINS

1. Adequate supply of raw materials.

2. Little or no influence of non-aerospace markets on quantity or quality of resins available.

3. Influence on non-aerospace markets on the quality and quantity of resins is undetermined.

4. Availability of commercial P.I. over the next 5-20 years depends upon the market demand.

5. In regard to government regulations, the Environmental Protection Agency regulations state that you cannot exceed a discharge of 15 lbs. in any one day or 3 lbs. in any one hour of heat-polymerized organic material into the atmosphere unless said excess has been reduced by at least 85%.

C. MANUFACTURING PROCESSES AND EQUIPMENT

1. Status of Processes:

a. Organic synthesis in commercially available processing equipment.

b. Prepreg tape production includes both wet dip and hot melt coating of reinforcements with polyimides.

c. Specifications for resins, prepregs, and cured laminates have been established for most commercially available polyimides. Individual specifications for specific resins are established according to the requirement.

d. QC and NDT methods include, QC - IR Scan, TGA, DTA; NDT, x-ray and ultrasonic.

2. Status of Equipment Required for:

a. Resin Manufacture

Sufficient processing equipment available with no difficulty foreseen in expanding facilities.

b. Prepreg Tape

No shortage on coating equipment.

c. Large Structural Components

Large autoclaves available at many aerospace firms.

d. NDT Large Composite Structures

X-ray - ultrasonic

3. Any Major Problems Associated with:

a. Manufacturing Specs. - None

b. Fabrication of large structures - None generally, except for a few addition systems which require 200 psi minimum or must be utilized in compression molding to realize optimum properties.

D. PROPRIETARY NATURE OF PI RESINS

1. No problem in establishing adequate specifications.

2. Availability of resins over 5-20 year period dependent upon market demand.

E. LIMITATION ON PI RESINS

1. Maximum use temperature of addition PI, around 550°F. Maximum use temperature of condensation type polyimides; around 650-700°F short time exposures.

2. Long term durability of addition type polyimides are limited to 500-550°F for a duration of 1,000 to 2,000 hours. However, one source shows approximately 70% retention of physical properties after 5,000 hours at 500°F. The condensation types exhibit good retention of properties after 2,000 hours up to 625°F prior to significant degradation.

3. Degree of difficulty in manufacturing large complex structures is limited only by the capacity of the available equipment. Some polyimides require high pressures and temperatures to demonstrate optimum properties.

F. NEW RESIN SYSTEMS

1. Some proposed competitors to polyimides are polybenzimidazoles, polyphenylenes, polyquinoxylines, polypyrolones, polysulfanes. However, none of them appear to have the overall thermal capability and strength of the polyimides. Ciba-Geigy has recently marketed a phenolic "analog", a condensation type resin that reportedly has excellent thermal stability at long time exposures to 250°C (482°F) - and

features epoxy-like processing characteristics either in vacuum bagging or autoclave molding. They also have developed a proprietary resin, designated only as NCNS which supposedly processes like an epoxy with reported excellent intermediate range 500-550°F properties.

G. PRICE

1. Currently available polyimide resins vary in price from $10-60 per pound.
2. Graphite/polyimide prepregs, both unidirectional tape and fabric vary from $100-300 per lb. dependent on quantities purchased.
3. The new experimental type resins such as Hughes' HR-600 is available at approximately $2,000 per pound.
4. There are no projected price increases for the commercially available types other than normal inflationary increases. Future prices on the newer and/or experimental types will, of course, be reduced based on their "successes" when they venture into the "commercial phase".

SUMMARY

The key issues regarding current graphite-polyimide technology on which Space Division will base its discussion are summarized as follows:

(1) There is an adequate supply of both condensation and addition type polyimide resin systems that exhibit excellent physical property retention at long term exposures to 500°F. These systems generally have good processing characteristics for adaptation to standard feasible manufacturing practices.

(2) Some condensation type polyimides feature good durability to long time exposure at 550°F, intermediate exposure to 600°F and a fair retention of properties at 700°F for short intervals.

(3) The addition types produce laminates of significantly lower void content but are limited to long term exposures to 500°F and intermediate term exposures to 550°F. It would follow that because of the lower void content they should feature superior resistance to high moisture or fuel environments in regard to degradation of properties under these conditions.

(4) Most materials purchased or samples received to date at SD utilizing the various types of PI impregnated on graphite unidirectional tapes exhibited poor qualities in terms of consistent resin control (including high and low concentrated areas, volatile content and degree of tack), tow separation, catenary, cross-over, etc.

(5) Some data available on the more recently developed additive-type polyimide polymers indicates superior thermal resistance. However, this information was developed on laboratory type laminates fabricated with relatively complex processing techniques and extended curing and post-cure cycles. These materials must also be proven under feasible, realistic manufacturing conditions.

The future of polyimide resin development availability and price reduction is dependent on expanded usage in both the aerospace and commercial industry. Future hypersonic aircraft will be seeking advanced composites materials with good thermal stability at 700°F. As to commercial adaptation, the development of polyimides began with seeking new hi-temperature varnishes for electronic components. These have potential applications in terminal boards, generators, coil forms, condensors, compressor blades, etc. Further commercial applications are possible in the field of "fireproofing" aircraft, boat or dwelling interiors.

One of the limiting factors that exist in the use of polyimide composites is in structures necessitating bonded joints and fabrication of honeycomb sandwich panels. There are only one or two commercially available polyimide adhesives at the present time, with questionable structural integrity at the 500°F level. There are a few new or experimental adhesives that have shown promise in this temperature realm, one a

Dupont 9622 system which is reported to retain a 1000 psi nominal lap shear strength of 1000 psi at 500°F after 1000 hrs. at 600°F; and the Dupont NR150 thermoplastic polyimide which though exhibiting lap shears of 2800 psi at 500°F on titanium/titanium substrates realizes only about 500 psi on carbon/graphite to steel bonds. Thus, the development of polyimide adhesives showing hi-temp capabilities should be pursued immediately if graphite/polyimide composites are to be used in future 600°F applications.

The application of the polyimides to sandwich panels would also require development of hi-temp splicing foams for core splices and syntatic foam fillers for panel edge filling.

In addition, associated processing materials are a necessity in order to fabricate laminated and bonded graphite/polyimide structures. This is in reference to the development or proven capability of existing materials to be used as vacuum bagging films, bag sealants and mold releases for the hi-temperatures processing parameters required.

TRW EQUIPMENT RESPONSE

APR 7'75

GRAPHITE/POLYIMIDE TECHNOLOGY ASSESSMENT

WILLIAM E. WINTERS
TRW EQUIPMENT
CLEVELAND, OHIO

INTRODUCTION

As a major fabricator of airfoils for gas turbine engines, particularly large fan blades, TRW Equipment has been keenly aware of the potential of composite materials not only for blading but other engine components as well. Programs of materials and hardware fabrication development in both resin and metal matrix composites have been pursued for at least 8 years. Although much auto and hydroclave experience is available at TRW, the application of structural composites to airfoils demands ultra-precision necessitating primarily die molding fabrication techniques. Also, because of rapidly rising temperatures in a jet engine, development efforts have been concentrated on high temperature composites, particularly polyimides. As a result, considerable experience in polyimide composite technology has been established at TRW.

As a part of this effort, TRW Equipment has been funded by NASA-Lewis to develop and optimize the processing parameters for a unique approach to forming PI composites. This concept involves the in situ Polymerization of Monomeric Reactants (PMR) directly onto the reinforcing fiber. After two years effort, PMR polyimide composites have been developed into viable materials of construction

and demonstrate a number of distinct advantages over other polyimides. Since there has been limited experience with PMR polyimides outside NASA-Lewis and TRW Equipment laboratories, the response to the subject questionnaire on Gr/PI will be directed primarily as an assessment of PMR polyimides. The discussion will, however, be initiated with a few brief and general statements about other polyimides based on TRW experience:

- Condensation Type - Generally good high temperature property retention (600°F) but extremely difficult to process to avoid precipitation and high void contents. This type system has never been mastered at TRW using die molding or clave curing.
- Addition Type (bismaleimide) - Extensive laboratory and hardware experience indicates ease of processing approaching that of epoxies. However, highly crosslinked polymers result in brittle matrix causing severe residual stress microcracking in complex oriented composites and poor translation of fiber properties in off-axis loading.
- "A" Type Addition PI - Can be fabricated into void-free composites but require very rapid heat-up rates precluding thick sections and autoclave curing. Use temperatures are limited to 550°F except for short duration.
- Thermoplastic Type - This type PI can be fabricated into void-free composites but require care in eliminating NMP

solvent and an elaborate stepwise temperature/pressure cure up to 800°F (NR-150B2). Resin has unusually high ductility and composites are thermo-oxidatively resistant and retain high percentages of properties over long term high temperature exposure. Thermoplasticity offers post-forming opportunities.

ASSESSMENT OF PMR TYPE POLYIMIDES
(PER QUESTIONNAIRE OUTLINE)

A. Polyimide Matrix Resins

1. Commercial Availability - PMR are addition polyimides similar in chemistry to the "A" type. They are not commercially marketed at this time although the constituents are readily available. The constituents are free flowing powders that are readily dissolved or esterified in methanol solvent.

2. Significant Characteristics - PMR PI's are readily formulated, can be easily tailored in molecular weight to fit particular requirements, form very low viscosity impregnating solutions, use a low boiling low toxicity solvent, and are easily and reproducibly processed into void-free composites. Primary effort has been with die molding, although 200 psi autoclave molding has been proven feasible. Long term exposure data indicate 60-80% retention of room temperature properties when tested at 600°F after 1000 hours at 600°F. Environmental effects are similar to other polyimides. Health hazards involve only the limited toxicity of methanol.

The resin is produced by simple mixing of the diamine, pre-esterified (refluxed) dianhydride and end cap. The low viscosity solution ensures fiber wetout during impregnation and the low boiling solvent allows developing appropriate drape and tack with mild or even room temperature "B" staging conditions.

Rapid solvent evaporation causes rapid dryout of prepreg in handling which can be reconstituted with additional solvent application or the use of higher boiling alcohols or other solvents. Curing is in two steps, an imidization at 250° to 400°F for 1 to 3 hours followed by a cure at 550° to 600°F. Unlike other "A" type PI's, extended gel time permits heat-up rates of 10°F/minute or less. Limited autoclave experience exists but structural components should be achievable given 550° to 600°F clave or heated tool capability. Excellent composite properties have been achieved with high strength and high modulus graphite and with glass reinforcements.

3. Five Year Commercial Availability - The concept was developed by NASA and hence is available to the public. Because of the many advantages of PMR polyimides and versatility available, it is predicted that a commercial form will be available within 5 years.

B. Availability

Constituents of PMR polyimides are now readily and commercially available from several sources within the U.S.A. No OSHA or EPA regulations restricting the use of PMR polyimides are known other than the use of methanol for which the toxicology is well established. Non-aerospace markets for polyimides including PMR are expected to be limited. Changes in the state of the economy are not expected to have effects. In 5 to 20 years,

polyimides and PI composites can be expected to be engineering materials of construction available in many forms from many sources.

C. Manufacturing Processes and Equipment

1. Resin and Prepreg Processing - Producing resins requires only esterification of two of the constituents both of which are off-the-shelf materials. Esterification of the end cap requires carefully controlled process but laboratory procedures have been established which can be scaled up without difficulty anticipated. The dianhydride is esterified with simple refluxing equipment. The resin is formulated by dissolving the pre-weighed constituents in solvent all of which are readily soluble. The solutions are stable for at least two weeks at room temperature, but because they are so readily prepared, they can be prepared daily as needed.

Prepreg to date has been readily prepared by drum winding. Low viscosity solution may require modification of conventional continuous tape impregnation methods. Quality control of resin is easily achieved with purity and melting point specifications on constituent materials. Specifications for prepreg and composites are comparable to other PI's or epoxies.

2. Fabrication and NDI Facilities - Die and press molding require only conventional tooling and platen press equipment.

Because of the 550° to 600°F cure temperature, large structural components require high temperature autoclaves or integrally heated tooling. Ultrasonic "C" scan techniques have been most effective in evaluating PMR as well as other composite structures.

3. Problem Areas - No problems are anticipated in providing manufacturing specifications. Large structural components will necessitate development and optimization of autoclave cure schedules for PMR composites as well as higher temperature facilities than used for epoxies.

D. Proprietary Nature of PMR

The availability of this NASA development to the public may, in fact, inhibit the development of proprietary formulations. However, the great versatility of the concept offers opportunity for resin suppliers to formulate compositions having unique characteristics over the next several years.

E. Limitation of PMR

Discussed in previous sections.

F. New Resin Systems

Although many high temperature resins other than polyimides are under development, none are seen supplanting polyimides in the near or intermediate term. Polyimides themselves present a severe challenge to the fabricator compared to epoxy or polyester materials. Other resins of which we are aware and familiar will

represent a next higher degree of complexity and processing difficulty. The polyimides offer at least 550 to 600°F capability. It is not expected that any organic resin will exceed long term 700°F capability. The price for the added 100° will be exceedingly high.

G. Price of PMR

1. Constituents for PMR-15 polyimide have been procured in laboratory quantities for $30/lb of cured resin. Preliminary surveys indicate that, in large quantities, a cost of $5-10/lb can be expected. Cost of prepreg would be commensurate with the resin and fiber costs compared to other epoxy or PI materials. Composites and components made from PMR resin containing materials should be comparable or only slightly higher cost than for epoxy composites. Other than materials cost, the added expense with PMR will result from more sophisticated bag and sealing materials, tooling (if heated tooling is used) or in high temperature autoclave facilities.

2. The added costs in item 1. above can be attacked by developmental effort in low cost, high temperature tooling approaches and in the development of economical integrally heated tooling techniques. For lower temperature systems such as epoxy, TRW has developed integrally heated, multi-station, temperature controlled tools for highly complex composite fan blades. The cost of these tools, which are adequate for prototype and

limited quantity production, have been found to be approximately one-half that of hard tooling.

SUMMARY

While a number of polyimide resins are available for use in structural composites, all are plagued with problems and limitations compared to more conventional and accepted epoxies. The PMR system offers many advantages compared to other PI's including ease of preparation, low viscosity solutions, improved performance, low cost, greater safety, versatility in composition and cure schedule selection. Quality composite hardware can and has been produced using die molding techniques. Although feasibility has been demonstrated for autoclaving PMR composites, additional development is necessary in this area. The primary disadvantage in clave curing PMR is the need for high temperatures for which limited facilities are available.

WHITTAKER RESPONSE

WHITTAKER RESPONSE

MAR 5 '75

PRESENT STATUS OF GRAPHITE-POLYIMIDE COMPOSITE MATERIALS TECHNOLOGY

FOREWORD

This review of the present state of the art of graphite/polyimide and polyimide adhesive technology was prepared by Whittaker Corporation, Research and Development Division, in response to a request from the McDonnell Douglas Program Office. The effort is in support of the Materials Application Branch at NASA Langley Research Center through their System Design Studies Program (NASA Contract NAS1-12436), and is complementary to the Polyimide Technology Assessment Conference to be held at the Williamsburg Lodge Conference Center, Williamsburg, Virginia, on March 17, 18, and 19, 1975.

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SUMMARY

The basic thrust of polyimide technology has been twofold; condensation reaction type resins and addition reaction type polyimides. An in-depth review reveals that serious, distinct, and quite dissimilar problem areas plague both approaches. Efforts to avoid these difficulties have met with only limited success.

An alternate approach involving the use of high temperature stable thermoplastic polymers in adhesive and composite applications shows promise but requires developmental effort to realize its potential advantages. Present adhesive/composite PI technology is inadequate to meet advanced aerospace criteria (i.e. processing compatible with present production capabilities combined with long term, 600°F service) as presently defined by NASA-LeRC.

General problems involving economics, raw materials shortage, proprietary systems, etc., are also discussed at some length.

A. POLYIMIDE (PI) MATRIX AND ADHESIVE RESINS

A large number of commercially available adhesive systems and matrix resins based on polyimides (PI) have been offered in recent years. The thirty-odd systems discussed below can be divided into two main categories, i.e. addition type and condensation type materials; and a minor category, i.e. thermoplastic materials. Within these three divisions, the processing requirements, handling characteristics, attributes, and drawbacks are, in general, quite similar. To facilitate this discussion, avoid an unnecessarily repetitive and protracted dissertation, and maintain a sharp focus on key areas of interest, the three PI divisions will be dealt with separately. General characteristics will be outlined, members of the groups will be identified, and exceptions or unique characteristics of individual resin systems will be discussed.

A.1. Condensation Polyimides

The first commercially available PI adhesive and matrix resins were exclusively condensation type polyimides. The standard reaction of an aromatic diamine with a dianhydride yielded the amic acid form. This form was supplied as a varnish in NMP, DMF, DMAC, or a mixture including one or more highly polar solvents. Adhesive prepreg or reinforced tape can be readily prepared from these amic acid solutions using standard techniques developed for epoxy based systems. Prepreg has good drape and tack and exhibits handling characteristics similar to epoxy based material, primarily as a

result of residual solvent. Conventional press, autoclave, or vacuum bag cures may be utilized, followed by oven postcuring to temperatures exceeding the intended end use temperature. The maximum use temperatures for condensation polyimides are:

Short term	(<100 hours)	650 - 750°F
Intermediate	(100 - 1000 hours)	550 - 650°F
Long term	(>1000 hours)	450 - 550°F

The fully cured polyimides are relatively inert chemically, exhibit excellent resistance to vacuum and radiation exposures, and are for all practical purposes insoluble.

These highly desirable characteristics are, unfortunately, balanced by two major and extremely serious drawbacks. The first problem is that the amic acid form of prepolymer is hydrolytically unstable. Figure 1 shows a typical hydrolysis reaction resulting in chain scission and finally nylon type salt formation. This final step is essentially irreversible and results in grainy, weak, low molecular weight, precipitated polymer. This tendency is aggrevated by further factors:

a. The hydrolysis is acid catalyzed; therefore the amic acid itself provides a catalyst for hydrolysis.

b. The most desirable solvent systems (those involving NMP) are hydroscopic and, in fact, excellent desiccants, and so readily capture atmospheric moisture and promote hydrolysis of the polymer.

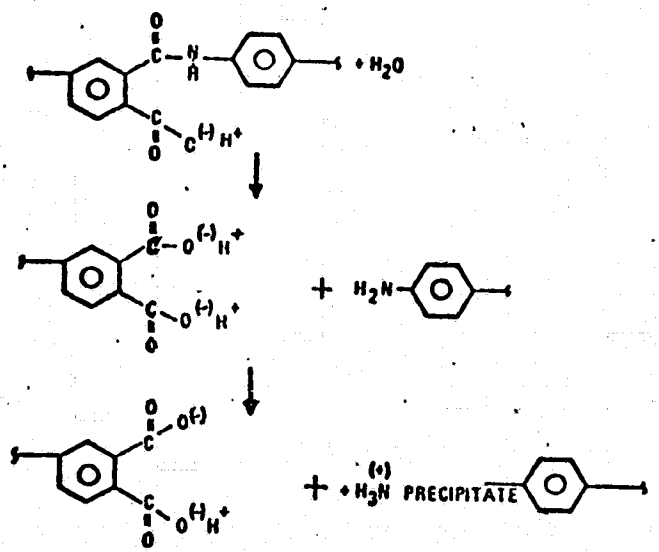


Figure 1. Typical Hydrolysis Reaction

c. As normal shelf aging occurs, condensation products including water are released from the resin itself and so aid in degrading the prepreg.

These resins (prepolymers) are, therefore, extremely sensitive to any exposure to moisture at any time in their history. It is not surprising, therefore, that major batch-to-batch variations occur, similar processing procedures yield dissimilar results, and the resin the fabricator receives may be quite different than that shipped by the resin producer or supplier.

The total end effect, i.e. the inability to generate reliable, reproducible satisfactory bonds or parts from commercially available prepreg, is a serious and major drawback and is the primary reason that polyimide bonding was discarded as a viable concept in Boeing's ill-fated SST program.

The most successful attempts at reducing this problem involve the use of "controlled flow" or amic ester based prepolymer as an alternative to the amic acid. The ethyl ester form commonly used reduces the hydrolysis problem significantly, but far from completely. Condensation imide prepolymers remain extremely sensitive to moisture and exhibit major batch-to-batch inconsistencies.

The second major drawback to condensation PI materials is that, as inferred by the same "Condensation PI," large amounts of volatile materials are condensed during polymerization and evolved during final cure. This leads to a myriad of processing difficulties that can only be overcome, if at all, by expensive, slow, tedious, demanding, and in general, highly undesirable techniques. A few examples should make the point painfully clear.

The bonding of large area metal-to-metal sections with condensation PI resins is precluded. The volatiles evolved literally rip apart such a bond when any attempt is made to fabricate sections other than thin strips. A possible solution is to drill holes at one-inch centers to provide escape paths for the trapped volatiles. The resulting penalty in time and money makes the concept extremely unattractive. Similar problems with sandwich structure lead to the use of perforated core, hand application of adhesive, 2 or 3 stage bonding, and unreliable results.

With composite applications, a formidable set of problems arise that can be attributed to volatile evolution, such as excessive porosity. Thick parts become extremely difficult or impossible to fabricate. If a reasonable heat-up rate is not maintained (a problem in itself with large production hardware) and if the bleeder system does not function efficiently, the evolving water hydrolyzes the PI, nylon type salts form, polymer precipitation occurs, and

the part is ruined. Expensive, slow, exacting, and numerous pre-compaction cycle techniques may be used; highly staged, boardy prepreg may be utilized, but results are always in question. Tooling, bleeding geometries and materials, heat-up cycles, pressure applications, etc., must be carefully and accurately matched and controlled for each individual part in order to have a reasonable chance of success (assuming this batch of polymer is the same as that you obtained last week). Needless to say, such techniques are economically extremely unattractive and do not lend themselves to a manufacturing or a production environment.

Other lesser problems exist with most of the condensation polyimides. The porosity resulting from volatile evolution provides easy access for moisture to enter the composite. While a significant degree of hydrolysis may or may not occur, the moisture does plasticize the PI matrix. This leads to the well-known "10 minute dip" phenomenon in testing PI adhesive or composite specimens. Elevated temperature performance is severely degraded. In systems where no actual hydrolysis occurs, the moisture may be driven off by heating and full performance restored. The significance of the phenomena when applied to an aerospace vehicle aerodynamically heating as it lifts out of a high humidity environment has not been determined.

Other problems, such as toxic solvents or additives and carcinogenic monomers, apply to specific systems and will be discussed

below as appropriate. The following table lists the major commercially available condensation polyimide products.

TABLE 1

COMMERCIAL CONDENSATION POLYIMIDE SYSTEMS

Description	Source	Use	Product Form
Skybond 700	Monsanto	Matrix Resin	Solution
Skybond 703			
Skybond 709			
Skybond 710			
F 170	Hexcel	Matrix Resin Adhesive	Prepreg
F 171			
F 172			
F 173			
F 174			
BPI 373	Brunswick	Matrix Resin	Prepreg
Nolimid A380	Rhodia	Adhesive	Prepreg
FM-34	American Cyanamide	Adhesive	Solution, Prepreg
951	Hexcel	Adhesive	Solution, Prepreg
4701	Du Pont	Matrix Resin	Solution
NR-150A	Du Pont	Matrix Resin	Solution
NR-150B			
NR-150A2			
NR-150B2			
NR-150AG	Du Pont	Adhesive	Solution

A few resins listed in Table 1 are of particular interest as they represent attempts, more or less successfully, to circumvent the problems inherent in condensation polyimides. The first of these is the Brunswick BPI 373. This system is essentially a highly staged version of Monsanto Skybond 703. The basic approach is to advance the PI, drawing off as much solvent and condensation volatiles as possible from the prepreg before assembling and curing the final part. Although large parts have been made with such techniques, there are obvious major drawbacks. The prepreg becomes boardy and stiff, with almost no drape or tack, and thereby extremely difficult to work with. High pressures are required in many cases. If autoclave cures are used, a multiple-stage curing technique is employed. A few plies at a time are applied and a full cure cycle run for each application. The time and labor involved make such an approach prohibitive for most production programs.

The Monsanto 710 system is an example that offers processing advantages over most other condensation polyimides. This system uses a mixed solvent containing ethanol, xylene, and NMP. The PI is quite soluble in the mix, even as molecular weight builds up. In most cases, the resin precipitation problem common to other condensation PI systems can be avoided. This increased solubility also allows the prepreg to remain tractable even after some condensation products are removed. To capitalize on this feature, numerous precompaction cycles are used to build up thick laminate assemblies.

The system retains good handling characteristics similar to epoxy based materials. Unfortunately, unlike epoxies, about 10% residual volatiles remain in the 710 at this point. If close control is maintained at all times on heat-up rate, pressure application, and other processing parameters, and the design of the tool, the bleeder system, and the vacuum bag are carefully and painstakingly matched to the particular part fabricated, a good part may be produced. However, any error in fabrication technique, or any batch-to-batch variations in the polymer may result in a ruined piece of hardware. The only answer may be to review the complete set of processing/ tooling/bleeder/cure parameters to match the new resin batch.

Attempts have been made to control (i.e. Q.C.) the 710 resin through an acid number determination and physical property measurements, but these have met with less than complete success. It is difficult to justify considering this approach as compatible with a manufacturing/production environment where costs must be controlled and schedules met.

The NR-150 series of resins from Du Pont offers perhaps the most promising approach to circumventing the problems of condensation polyimides. Many classify these resins as thermoplastic materials, which infers that a fully polymerized thermoplastic is used to fabricate parts and shapes through physical change only. This impression is misleading and incorrect. The NR-150 resins are true

condensation polyimides supplied in solution. Du Pont* reports these resins to be relatively stable in solution and to exhibit excellent shelf life, unlike other polyimides. The disadvantage is that increased volatiles are evolved and must be dealt with during cure as the condensation reaction proceeds. For best results, prepreg should be staged to a boardy or near boardy condition (<11% volatiles) to control excessive flow and problems associated with excess volatile evolution. Curing and processing parameters are not straightforward or as yet well defined. Again, expensive, painstaking bleeder techniques are required. The big advantage is that the final polymer retains a high degree of thermoplasticity at termperatures above the T_g. By applying enough pressure above the T_g, the voids or porosity formed during cure may be molded out of the laminate, resulting in a low void, high quality finished part. The obvious disadvantages to such techniques are that autoclave requirements as well as sealers, bags, etc., approach the limits of present state of the art and are rarely if ever found in a production environment. The alternative is carefully tooled matched metal dies and large heated presses which involve a considerable expense.

Even though such requirements are not extremely attractive, the overall problems are not insurmountable and the NR-150 resins may be the most promising of all condensation polyimides. An added bonus

*Dr. Hugh Gibbs, private communication.

is that the NR-150B and B2 resins have exhibited outstanding thermal-oxidative stability, definitely superior to the other condensation systems in use. It may be possible to show actual long-term 600°F service capability for these materials, unlike Monsanto 710 and most other condensation polyimide resins.

A.2. Addition Type Polyimides

In order to avoid the major problems found with condensation polyimides, a new approach was developed by some resin suppliers. The technique incorporated reactive double bonds into the PI. The PI was completely imidized prior to the final cure, which consisted of an addition type polymerization. In this way, the imidized resin was hydrolytically stable as prepreg and no volatiles would be evolved during the final cure. Thus the two major problem areas associated with condensation polyimides could be avoided in one stroke.

Figures 2 and 3 give the chemistry of P13N and Kerimid 601, which are representative of the approaches used for addition polyimides. Table 2 lists current addition type polyimides.

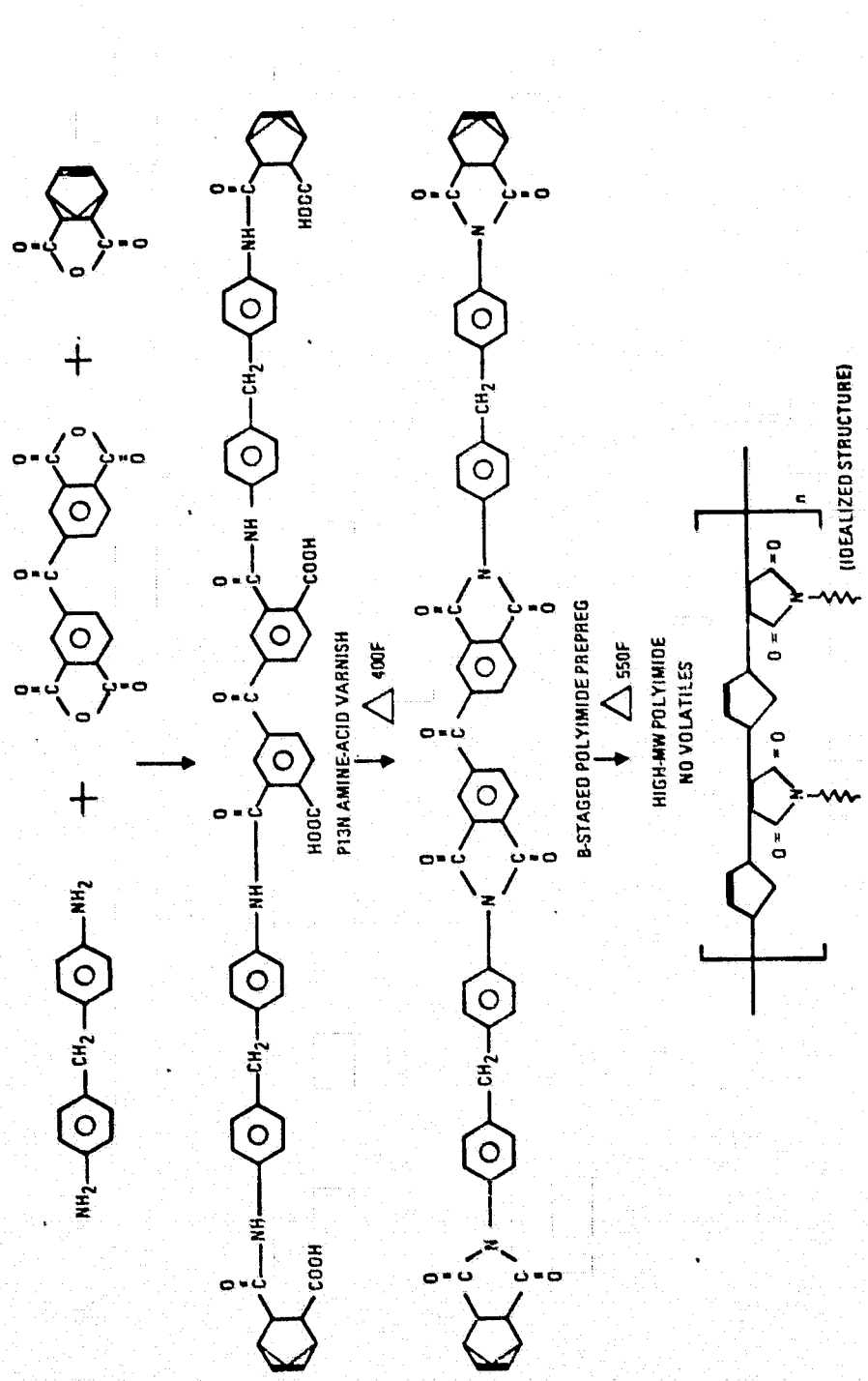


Figure 2. P13N Polyimide Cure

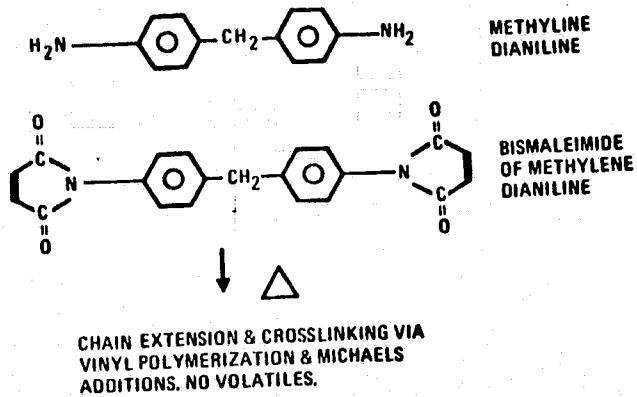


Figure 3. Kerimid 601 Chemistry

TABLE 2

ADDITION TYPE POLYIMIDES

Description	Source	Use	Form
P13N P105A	Ciba-Geigy	Matrix Resin	Solution
Kerimid 601 Kerimid 353	Rhodia, Inc.	Matrix Resin	Solution
F 175 F 176 F 177 F 178	Hexcel	Matrix Resin Adhesive	Prepreg Tape
3003	Du Pont	Matrix Resin	Prepreg Tape
PMR 15	-	Matrix Resin	Solution

The emergence of new addition type polyimides follows an interesting pattern, perhaps shaped by difficulties that arose in early versions of these resins. The P13N resin system was initially developed by the TRW Systems and later produced and marketed by Ciba-Geigy Corporation. The resin was usually completely imidized to a boardy, stiff prepreg. An amic acid version with good drape and tack was also offered, but this obviously retained the problems of hydrolytic instability, etc., associated with condensation PI prepreg. During cure, the resin passed through a melt phase where flow and consolidation occurred, and then the addition polymerization followed. The main difficulty with P13N was that the melt and addition reaction temperature ranges overlapped. A hot press or an exceedingly high heat-up rate was required to produce quality parts. This precluded use of most autoclave cure cycles and made the fabrication of large parts extremely difficult if not impossible.

In order to overcome the problem with P13N, P105A was developed by Ciba-Geigy. Here, the inclusion of thiodianiline in the polymer resulted in a stable melt phase at a temperature safely below that required for imidization. Unfortunately, when thiodianiline appeared on OSHA's list of carcinogens, the material became far less attractive to market and is no longer being offered. The P105A did, however, exhibit potential for autoclave curing and was a definite improvement over P13N.

Meanwhile, Rhone-Poulenc in Europe was developing polyimides based on bismaleimide chemistry. The Kerimid 601 presently marketed by Rhodia, Inc., is the most well-known version. Initially, General Electric had marketed this polymer as Gemon L. It was reported, however, that when DMF solutions were used, as with Gemon, elevated temperature performance was severely degraded to the point where even 450°F aging was not satisfactory. In marketing Kerimid 601, NMP solutions only were offered. While performance improved, a serious problem was discovered. As heat was applied to the part, it cured from the outside in, sealing the surfaces. A small amount of residual NMP was retained by the Kerimid. As a result, heating and postcure resulted in severe delaminations wherever thick, large shapes were contemplated. As a result, the Kerimid 601 is no longer recommended for use in continuous graphite reinforced composites by Rhodia.

Rhone-Poulenc has recently brought out a new material based on bismaleimide chemistry to overcome this problem. Kerimid 353 is a hot melt PI which allows prepregging from the melt phase. No solvent is ever involved. The performance of Kerimid 353 has yet to be established. While avoiding the solvent problems that plagued Gemon L and Kerimid 601, it is expected to share the many drawbacks common to addition polyimide resins that will be discussed in detail below.

The Hexcel polymers are formulations based on similar chemistry. Kerimid 601 is used in some cases, while a hot melt type bismaleimide is used in the remainder. The remarks above for the Kerimid materials apply equally to the Hexcel addition PI products. Some legal questions between Rhodia, Inc., and Hexcel remain to be resolved at this time.

The Du Pont 3003 matrix system is included at this point for want of a suitable category to place it. The 3003 is a proprietary polymer, which Du Pont describes as not a true addition type but similar in processing and handling. It also shares the drawbacks of addition polyimides and evolves some volatiles during processing.

The discussion of addition polyimides has followed the development of individual systems without generalizing on the class as a whole. Although they first appear attractive, some serious major drawbacks cannot be overlooked. The first, and one of the most serious, is reduced thermal-oxidative stability. The use temperatures are as follows:

Short term use temperature	(< 100 hours)	550 - 600°F
Intermediate use temperature	(100 - 1000 hours)	450 - 550°F
Long term use temperature	(> 1000 hours)	400 - 500°F

This is significantly poorer performance than that exhibited by condensation polyimides as a group and may preclude the consideration of addition type polyimide for use in advanced aerospace applications. The P13N type systems fall at the upper end of the above range while the bismaleimides are found at the lower end.

The lower amount of aromatic, stable structure and higher amount of aliphatic crosslinked structure in the polymer when compared to linear condensation polyimides also results in another problem. The addition polyimides are highly crosslinked and, therefore, more rigid (less tough) than condensation PI. Elongation is poor, transverse properties are low, and the resins are quite susceptible to microcracking during cure. These are serious problems that appear to be inherent in addition PI.

Although environmental aging characteristics have been reported as good, recent work at Whittaker R&D and elsewhere indicates that problems exist analogous to those of condensation polyimides. Water is absorbed through microcracks and other discontinuities. Although little or no hydrolysis occurs, the moisture plasticizes the matrix and greatly reduces elevated temperature performance. The process is reversible as the water is readily driven off by heating. Holding a test specimen 20 or 30 minutes at temperature before testing completely misses the problem, while loading and heating simultaneously (which may occur in actual service) shows severe performance degradation.

The poor elongation of these resins also manifests itself in poor strain-to-failure characteristics and reduces the appeal of these resins as engineering materials. As a class, the addition polyimides do not appear suitable for consideration in advanced aerospace.

A new development in addition PI technology may prove the lone exception to the above statement. Work at NASA-LeRC on Polymerization of Monomeric Reactants (PMR) approaches to P13N chemistry led to the development of PMR 15 polyimide. Here, stable solutions of monomeric reactants are used to produce prepreg. The usual process involves placing the layup directly in a heated press. Bumping techniques are used to allow volatiles to escape as melting, imidization, and the addition reaction quickly follow. Excellent parts have been fabricated with such techniques. PMR-15/HM-S laminates* exhibited outstanding stability to 1000 hours aging at 550°F and 800 hours at 600°F which is extremely impressive considering the structure of the polymer.

It is not clear, however, how such processing concepts can be adapted to large aircraft hardware. The problems of high heat-up rates, microcracking, poor elongation, etc., inherent in present

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*P. J. Cavano, Science of Advanced Materials and Process Engineering Series, 19, 653 (1974)

*T. T. Serafini and R. D. Vannucci, Proceedings, 30th Soc. Plastics Industry Conference, Washington, D.C., February 1975, Sect. 14-E, p.1

addition type polyimides remain to plague PMR-15. At this time, it cannot be seriously considered as a candidate for advanced aerospace applications.

A.3. Thermoplastic PI

A final category to consider is that of the thermoplastic polyimide. Such materials are fully polymerized resins that are processed through physical, not chemical change. (Note that the NR-150 series does not fit this description and is properly treated with condensation polyimides above.) The only commercially available material, Upjohn 2080, is proprietary and has major shortcomings. Maximum service temperature is 450 - 500°F; the resin loses thermoplasticity rapidly as it experiences high temperatures, and batch-to-batch variation has been excessive. The 2080 is not a viable candidate for large Space Shuttle applications.

A.4. Experimental Polyimides

Perhaps the only experimental polyimide of interest which may be commercially available in 5 years is the Hughes HR 600 resin. In this system, the PI* is acetylene end-capped, thus allowing a final cure to be affected without release of volatiles. Presently, the projected price of ~ $1,000/lb for HR 600 and unavailability has limited work with the resin. Some question exists as to

*A. L. Landis, et al., American Chemical Society, Division Polymer Chemistry Preprints 15 (2), 533 and 537 (1974)

whether the price will ever drop to commercial levels. The system is too new to be discussed in depth; however, real questions are raised concerning shelf life, elongation, microcracking, heat-up requirements, and other problems that remain to be resolved with the HR 600 polymerization.

B. AVAILABILITY OF PI RESINS

B.1. Raw Materials

The question of raw materials cannot be answered with certainty. Starting materials are dependent on the petrochemical industry and therefore on the world fuel situation. Increased fuel shortages and demands will logically interfere with the availability of materials. This is similarly true for epoxies and most other organic resin systems.

B.2. Government Regulations

The impact of government regulations is another unpredictable variable. OSHA regulations have already essentially killed P105A as a viable candidate system. Reactive aromatic amines as used in PI (and high temperature epoxies, etc.) are, by their nature, irritating, dangerous materials. EPA and OSHA requirements may very well result in significant cost increases for such chemicals and in some companies, deletion of these chemicals from their product lines. It may be significantly more expensive and/or difficult to obtain any or all PI, depending on new regulations and interpretations by government agencies.

B.3. Non-Aerospace Markets

The pressure of non-aerospace markets is certainly a positive factor on the quality and quantity of available polyimides. Work in circuit board applications, as coatings in high temperature applications, as varnishes, etc., has kept PI chemistry active. Certainly

the selection and quality of resins would be greatly reduced without present commercial applications. Similarly, new commercial applications would be a great shot in the arm, just as the golf shaft and other sporting goods applications have led to lower prices and improved quality in graphite fiber reinforcements.

In a less obvious sense, the PI themselves are being tailored to take advantage of starting materials that enjoy commercial application. A prime recent example is NR-150A2 and B2, which utilize widely available diamines instead of the small volume specialty diamines used in the original NR150A and B resins.

B.4. Economic Effects

The general effects of the changing state of the economy are readily apparent and the obvious comments need not be made here. Specific discussion is left to members of the panel with a detailed knowledge of the specifics involved.

B.5. Availability

The availability of current commercial PI resins in 5, 10, or 20 years is directly related to government regulations, profitability, the presence of a reasonable market. If the latter is not forthcoming, it is no great feat to predict that few will be readily available. The variables and assumptions involved in any production are of such a nature to render the predictions meaningless. Essentially, this point simply involves repetition and paraphrasing of discussions

B.1. through B.4. above. It does appear, however, that if no real applications can be found in a nearly ideal vehicle such as the Space Shuttle where weight savings and high temperature performance are at a premium, one wonders where or when, if at all, polyimide adhesive and composite technology has real application in the aerospace industry.

C. MANUFACTURING PROCESSES AND EQUIPMENT

C.1.a. Resin Production

The state of the art for producing resins is quite advanced. The chemistry is well understood, the reactions can be well controlled, and adequate Q.C. can be maintained if the effort is made to achieve such results. Rheological and spectroscopic techniques insure uniformity when properly applied. However, the expense and trouble of maintaining adequate Q.C. may or may not be assumed by the supplier; the level of effort appears commensurate with the pressure on the resin supplier.

C.1.b. Prepreg

As far as prepreg is concerned, modern continuous processing follows the well-established methods developed for epoxy based systems. While prepregging from solution is probably necessary and desirable with respect to condensation PI, such techniques result in severe degradation in the performance of addition polyimides (see discussion above). New hot melt techniques developed for epoxies are required for these resins. In addition, hot melt processing is faster, cheaper, and avoids major problems of pollution control (and subsequent OSHA or EPA involvement). Additionally, hot melt techniques are not necessary but are certainly desirable in processing high temperature thermoplastic systems.

C.1.c. Specifications

Specifications for cured laminates are quite definitive and generally adequate. This is in sharp contrast to the situation that exists for resins and prepreg. The reasons for this are not difficult to discern. In the former case, simple physical and mechanical tests may be applied to determine the properties of interest to the engineer, designer, etc. These specifications deal with a relatively inert, stable, nonvarying piece of material in a manner analogous to that used for handling steel, plywood, copper, or other common materials of construction.

In the case of resins and prepreg, definition of physical and mechanical properties is necessary, but far from sufficient, in the preparation of adequate specifications. These materials undergo chemical changes which drastically alter their character and may be brought on by exposure to heat, moisture, or simply extended ambient aging. In many cases the resins are proprietary, and the user preparing a specification has little if any knowledge of the chemistry involved with the system. Simple spectroscopic analysis, physical testing, and acid number titrations are far from adequate. The widespread and obviously apparent results are found in nearly all manufacturing or development programs involving PI. A recognition of the need for significantly improved and definitive specifications is certainly a prerequisite for successful major applications of these resins.

C.1.d. NDE and Q.C.

Q.C. and NDE for adhesive bonds and composite structures are, at present, slow, expensive, and/or inadequate. Techniques involving ultrasonics, liquid crystals, etc., may be effective in locating voids, delaminations, or disbonds. They are ineffective, however, in differentiating between strong and weak bonds, problems resulting from inadequate surface treatment of adherends in adhesive bonded structure, or inferior laminates with poor fiber wetting, low state of cure, poor molecular weight buildup, etc. Research is proceeding on more effective (and usually expensive) techniques, but these efforts still have a long way to go. Methods utilizing sampling and destructive testing still are the Q.C. backbone for production applications of composites or of bonded structure.

C.2.a. Resins, Prepreg, Components

The status of equipment for manufacturing resins and prepreg is certainly adequate. As discussed above, the chemical reactions are well known, long established, and can be controlled. The equipment required to produce prepreg from solution or from hot melt is well established and developed. New, large broadgoods laying machines, etc., are under development, but the emphasis is on faster, cheaper production, not on solving inherent problems with the concept. The fabrication of large structural components, however, is a laborious, expensive, painstaking, and antiquated procedure. Tape laying

machines are fine for simple, flat panels, but complex/contoured shapes render them of little use. Highly skilled hand layup and batch processing techniques are used with the resulting high costs, high scrap factors, and low production rates. The sensitivity of PI systems to processing parameters (703 and 710 are good examples here) greatly magnify the risk and the expense of such processing. No production program involving the fabrication of high quality large structural components from graphite/PI or utilizing significant large area or sandwich PI bonding has been successful to date.

C.2.b. NDE and Q.C.

The NDE and Q.C. of large structural components fabricated from graphite/PI or utilizing significant amounts of PI structural bonds are inadequate. Remarks made above concerning NDE and Q.C. apply here, only to a greater degree.

C.3. Major Problem Areas

C.3.a. Problems Associated with Establishing Adequate Manufacturing Specifications

(1) Knowledge of the polymer chemistry involved.

(2) Identification and definition of crucial resin parameters for the particular system in use.

(3) Development of efficacious in-house Q.C. testing to check the parameters identified and defined in (2).

(4) Close control of the resin history from synthesis

through cure.

(5) Development of effective NDE and Q.C. for adhesive bonding and large composite components.

The above are in addition to standard considerations presently used for graphite/epoxy and state-of-the-art manufacturing materials.

C.3.b. Problems Associated with Fabricating Large Structural Components

(1) Establishing adequate manufacturing specifications (see (a) above).

(2) Achieving adequate heat-up rates for addition type and PMR type resins (i.e. P13N, PMR 15, etc.)

(3) Maintaining close control over the myriad of processing variables effecting the quality of laminates fabricated from condensation PI resins (i.e. 703, 710, etc.)

(4) Achieving the temperatures and/or pressures required to fabricate good components from boardy polymer systems (i.e. PBI 373) or from those utilizing thermoplastic molding characteristics (i.e. NR-150 series, 2080).

(5) Avoiding out-time (shelf life) problems with almost all systems.

(6) Maintaining cleanliness and high quality surface treatments for bonded structure.

D. PROPRIETARY NATURE OF PI RESINS

D.1. Effect on Specifications

It is unlikely that adequate M&P specifications can be established without detailed knowledge of the polymer chemistry involved in the system. Problems that arise cannot be readily analyzed or solved; the manufacturer loses control of his manufacturing process. The truism that the resin supplier will perform adequate customer service has not held true. He is often understaffed, has insufficient R&D resources, and certainly does not have the driving incentive to investigate all aspects of the resin for a particular application using a particular set of processing equipment, with unique service requirements for the end product. The resin supplier is also unlikely to voluntarily adopt additional Q.C. procedures that will raise the price of this product and so render it less competitive with others on the market.

Communications problems simply add to the difficulties already present.

D.2. General Effects

The proprietary nature of some PI materials has led to the problems discussed in D.1., and is a major factor in the lack of success realized in PI programs. This is certainly a profound negative influence on the use of PI adhesive or prepreg and the subsequent long term availability of such resins. As an example,

one needs only look at the lack of development of condensation PI adhesives and prepreg in recent years and the reluctance of many prepreggers to handle such resins.

E. LIMITATION ON PI RESINS

The limitations on PI were discussed above in detail, both generally in terms of condensation and addition PIs, and specifically concerning individual resin systems.

F. NEW RESIN SYSTEMS

The discussion of points A through E above leads to the conclusion that serious difficulties and major obstacles are associated with all available polyimides. An obvious approach is to avoid PI chemistry altogether and choose an alternate resin. Unfortunately, as is the case with oversimplified solutions, this alternative is not so simple after all. Essentially, this approach involves finding a polymer with excellent thermal/oxidative stability at temperatures to 600°F combined with good toughness and elongation, one that gives off little or no volatiles during fabrication, one that can be readily processed and whose chemistry can be closely controlled under production conditions, one relatively insensitive to moisture and environmental aging, and one that can be made commercially available at relatively moderate cost. Note that the above criteria excludes not only PBI, BBB, PIQ, polybenzothiazoles, inorganic polymers, and other exotic systems, but also all PIs discussed above, with the possible exception of the NR-150 materials.

There is a class of polymeric materials that may meet the above criteria. High temperature thermoplastic resins exhibit great promise for use in adhesives and as composite matrix resins. If extended use temperatures of 450°F are adequate, this list must include polyarylsulfones, thermoplastic polyimides, linear poly-as-triazines, and polyphenylquinoxaline systems (PPQ). For the

purpose of this discussion, only materials with demonstrated 600°F capability will be considered. This narrows the list of polymers to PPQs. (Note: NR-150B2 may also be added to the list if sheet stock can be consolidated from fully polymerized tape using reasonable processing parameters, and if postforming of complex/contoured shapes from such stock is feasible. Such capability, while demonstrated for PPQ systems, has not as yet been established for NR-150B2 resins.)

Composites* were fabricated from a phenylquinoxaline copolymer and Hercules HM-5 reinforcement at the Boeing Company under a NASA contract that exhibited outstanding strength retention at 600°F after 500 hours at 600°F in air. In addition, PPQ titanium (6Al-4V) adhesive specimens also exhibited excellent strength retention at 600°F after 500 hours at 600°F in air.** Such performance is certainly impressive and in line with advanced aerospace requirements.

High temperature thermoplastics as a group exhibit good elongation and toughness. The problems of microcracking, poor strain to failure, low transverse properties, inferior fatigue life, and reduced ability to distribute stress that plague addition

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*P. M. Hergenrother, Applied Polymer Symposium, 22, 57 (1973)

**P. M. Hergenrother, J. Applied Polymer Science, 18, 1779 (1974)

polyimides are generally absent in high temperature thermoplastics. When used as an adhesive, PPQ has shown RT climbing drum peel strengths* of over 90 in.-lb/3-in. width on titanium (6Al-4V) adherend, a value 2 times better than that obtained with the best commercially available PI.

The high temperature thermoplastics can be processed as fully polymerized, high molecular weight materials. Since no further chemical reaction occurs and solvents are not required, the volatile problems inherent in addition polyimides do not exist. Similarly, since fully cured, inert resins are used, no problem of shelf life, hydrolysis, or prepreg instability need be considered.

Perhaps the greatest advantage of the high temperature thermoplastics appears in the simplification of processing and the resulting cost savings. If one starts with prepreg tape, tape laying machines may be used in almost all applications, since only flat panels are required. These layups may then be consolidated in simple, inexpensive heated flat presses, avoiding the need for expensive autoclaves, slow batch processing, vacuum bags, bleeder systems, etc. It may prove feasible to simply consolidate layups through hot nip rolls. Alternately, consolidated flat stock may be received directly from the supplier.

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*P. M. Hergenrother, SAMPE Quarterly, 3(1), 1 (1971) and AFML-TR-73-68 (1973)

Complex contoured shapes are then postformed directly from flat stock. Recently at WRD, hemispherical shapes were successfully postformed from PPQ matrix flat stock reinforced with woven Thornel 300 graphite cloth. Other structural shapes such as hats, channels, and angles were also successfully postformed from cross-plied continuous graphite fiber reinforced PPQ matrix stock. The The technique has been successfully demonstrated.

Discarding the concept of curing and getting the hardware manufacturer out of the polymer chemistry business has major advantages for everyone. The problem of specifications becomes much simpler, as flat stock can be ordered according to its physical and mechanical properties, just as metals are now routinely handled. Acceptance testing can be readily handled in a manner familiar to the fabricator. Actual manufacturing can proceed in a straightforward manner with no chemical reactions involved and in a manner analogous to that used for state-of-the-art metals and unreinforced thermoplastics.

The material supplier also has far greater control of the polymer and need not worry about placing chemically sensitive materials, whose reaction parameters must be carefully controlled, into the hands of workers untrained in polymers or polymer chemistry. The producer or supplier also then bears the responsibility of resin Q.C. and now has significant motivation

to produce a stable, reproducible product. The problem of proprietary materials is also minimized, since, as stated previously, only physical and mechanical performance at temperatures of interest concerns the fabricator.

The PPQs have also been shown to be relatively insensitive to moisture and show little degradation of elevated temperature performance. In work at Gulf General Atomic* PPQ films proved nearly impervious to water vapor and outperformed other polymers by a large margin. These resins were chosen to seal PI laminates from moisture in SST prototype applications at Boeing prior to the termination of the program.

The consideration of cost is presently a problem area with PPQ systems, but not as severe a problem as commonly believed. Present 600°F type PPQs may cost ~ $500/lb in small quantities, but projections show the cost dropping to ~ $30/lb when a sales volume of 100,000 lb/year is achieved.

Another drawback is that developmental work is required on the high temperature versions of PPQ systems. However, the efforts appear to be straightforward and direct in sharp contrast to the severe, perhaps insurmountable technical difficulties inherent in

*R. L. Riley, et al., Gulf Report No. EN-A-12473, prepared under Contract No. 14-30-3016 for Office of Saline Water, U.S. Dept. of Interior, February 1973.

most PI systems presently available. Whittaker R&D believes the development of these high temperature thermoplastics offers the opportunity to meet all performance requirements and eventually achieve significant cost savings, all at far lower risk than that involved in the pursuit of condensation or addition type PI technology. The impact of such development, if successful, would obviously greatly reduce th demand and the subsequent availability of PI for such applications.

G. PRICE

G.1.a. Raw Materials

In general, shortages of petrochemicals and the influence of OSHA or EPA regulations has and will probably continue to raise the price of raw materials. Just how severe these factors will become and how strongly the impact on the polymers will be cannot be predicted.

G.1.b. Resins

Common resins, produced in volume from widely used raw materials, will probably show an increase in price for the reasons discussed in G.1.a. above.

The resins which presently enjoy limited markets and require exotic, toxic, or simply different starting materials from those commonly used (i.e. NR-150 resins with hexafluoroacetone, PPQ systems) should see significant price reductions as and if their volume expands. Projections for these materials may approach the more common materials if sufficient markets develop.

G.1.c. Prepreg

The price of prepreg has stabilized or gone up slightly. Inflation, labor prices, and material costs all act in the undesirable direction. The reduced prices resulting from volume prepreg consumption in the sporting goods industry have stabilized

somewhat and new, significant markets are required before additional reductions will occur. If such markets do not materialize, effects of inflation, shortages, etc., will invariably force prices upward.

G.1.d. Graphite PI Composites

For the reasons given above, unless significant markets for these materials can be established, the prices will invariably rise. The one bright spot is that the use of high temperature thermoplastics and the resulting savings in manufacturing costs could significantly reduce the final cost of the graphite reinforced hardware.

G.2. General Cost Considerations

Section G.1. was answered in general as well as specific terms, with factors influencing the cost of materials identified. A repetition of this exercise would be superfluous in this section. The cost savings resulting from reduced manufacturing costs (i.e. high temperature thermoplastics) are one of the few bright spots in the overall cost picture. These savings appear to be real, as cost savings (as well as the expected weight savings for graphite reinforced thermoplastic structure) over conventional aluminum hardware have been projected in cost studies conducted on various Air Force and Navy sponsored programs.

THE MEETING B

Appendix B
THE MEETING

The attendance at the three-day Williamsburg conference was as follows:

Monday	3/17..... 21
Tuesday	3/18..... 16
Wednesday	3/19..... 18

The meeting agenda and a list of the attendees and their respective organizations are given in the following pages. The remainder of this section includes the unedited presentations that were made on the first day of the conference. A summary of the presentations, prepared by the chairman, Mr. Ira Petker, can be found in Section 2 of this report.

AGENDA B.1

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Appendix B.1

AGENDA

GRAPHITE-POLYIMIDE COMPOSITE MATERIALS
TECHNOLOGY MEETING
Williamsburg, Virginia

Colonial Williamsburg Conference Center		Room D-E (Lower Level)
Monday – March 17, 1975		
9:00 a.m.	Welcome	Dr. J.G. Davis, Jr. /NASA
9:09 a.m.	Introduction by Meeting Chairman	Mr. I. Petker
9:14 a.m.	American Cyanamid Presentation	Mr. R. Politi
9:48 a.m.	CIBA-GEIGY Presentation	Dr. S.S. Hirsch
10:17 a.m.	COFFEE BREAK	
10:37 a.m.	DuPont Presentation	Dr. H. Gibbs
11:07 a.m.	Monsanto Presentation	Dr. A.H. Markhart
11:37 a.m.	Composite Horizons Presentation	Mr. I. Petker
12:00	LUNCH	
1:08 p.m.	Whittaker Presentation	Mr. M.G. Maximovich
1:39 p.m.	General Dynamics Presentation	Mr. W.G. Scheck
2:08 p.m.	McDonnell-Douglas Presentation	Mr. R. Kollmansberger
2:38 p.m.	BREAK	
2:53 p.m.	Rockwell International Presentation	Mr. S. Yoshino
3:24 p.m.	TRW-Equipment Presentation	Mr. W.E. Winters
3:51 p.m.	Questions by Invited Attendees	Meeting Chairman and Participants
4:30 p.m.	General Planning for Tuesday's Meeting	Chairman
5:00 p.m.	Adjourn	

Tuesday – March 18, 1975

9:00 a.m.	Preview of Day's Events	Chairman
9:05 a.m.	Discussion of Key Issues	Industry Forum
10:30 a.m.	COFFEE BREAK	
10:45 a.m.	Discussions Continued	Industry Forum
12:00	LUNCH	
1:15 p.m.	Discussions Continued	Industry Forum
3:00 p.m.	BREAK	
3:15 p.m.	Discussions Continued	Industry Forum
4:15 p.m.	Adjourn	

Wednesday – March 19, 1975

9:00 a.m.	General Summary of Key Issues and Continuation of Discussions	Chairman and Panel Members
10:35 a.m.	COFFEE BREAK	
10:45 a.m.	Questions by Attendees	Chairman and Panel Members
12:00	Specific Recommendations for NASA	Chairman and Panel Members
1:00 p.m.	Adjourn (at Williamsburg)	Chairman and Panel Members
2:00 p.m.	Chairman's Informal Review of Sessions to NASA (at LaRC)	Chairman
3:00 p.m.	Adjourn	Chairman and NASA Personnel

ATTENDEES B.2

Appendix B.2
ATTENDEES

ATTENDANCE 17 March 1975

GRAPHITE-POLYIMIDE COMPOSITE MATERIALS CONFERENCE
WILLIAMSBURG, VA.

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	CONVAIR DIVISION	x1950
	P.O. BOX 80847	
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STAN YOSHINO	ROCKWELL INT.	213-922-2610
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ATTENDANCE 17 March 1975

GRAPHITE-POLYIMIDE COMPOSITE MATERIALS CONFERENCE
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ATTENDANCE 18 March 1975

GRAPHITE-POLYIMIDE COMPOSITE MATERIALS CONFERENCE
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GEO. R THOMAS	USAMMRC	617-923-3349
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John G Davis Jr.	NASA - Langley - Composites Section	804-827-2125

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ATTENDANCE 19 March 1975

GRAPHITE-POLYIMIDE COMPOSITE MATERIALS CONFERENCE
WILLIAMSBURG, VA.

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ATTENDANCE 19 March 1975

GRAPHITE-POLYIMIDE COMPOSITE MATERIALS CONFERENCE
WILLIAMSBURG, VA.

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PRESENTATIONS B.3

Appendix B. 3
PRESENTATIONS

The 10 presentations in this appendix were given at the Williamsburg Conference Center, Williamsburg, Va., on 17 March 1975. They are unedited and are presented in alphabetical order by company.

American Cyanamid	Mr. R. Politi
CIBA-GEIGY	Dr. S. S. Hirsch
Composites Horizons	Mr. I. Petker
DuPont	Dr. H. Gibbs
General Dynamics	Mr. W. G. Sheck
McDonnell Douglas	Mr. R. Kollmansberger
Monsanto	Dr. A. H. Markhart
Rockwell International	Mr. S. Yoshino
TRW Equipment	Mr. W. E. Winters
Whittaker	Mr. M. G. Maximovich

AMERICAN CYANAMID PRESENTATION

POLYIMIDES AND RELATED HETEROCYCLIC STRUCTURAL ADHESIVES

Robert E. Politi

American Cyanamid Company
Bloomingdale Plant
Havre de Grace, Maryland

INTRODUCTION

Although conventional polyimide (PI) adhesives have now been commercially available for about ten years, their capabilities and limitations are not fully understood by many materials engineers. PI adhesives are frequently considered for use in applications where the more easily processed and less expensive high temperature epoxy or epoxy-phenolic adhesives would be suitable. Conversely, although to a lesser extent, epoxy and epoxy-phenolic adhesives are sometimes considered for use in applications involving exposure conditions which far exceed their performance capabilities.

This paper is divided into three sections. The first section briefly compares the performance and processing requirements of conventional (ie. condensation reaction) PI adhesives to those of earlier types of structural adhesives. It is hoped that data presented in this section will be useful to the materials engineer in selecting the proper class of adhesives to evaluate for a given application.

In the second, and major, section of this paper, the processing requirements and performance of conventional PI adhesives is discussed in depth. The release of volatiles during cure is, of course, the major cause of processing problems with these adhesives. The proper use of bleeder systems, venting and vacuum to alleviate porosity and resin precipitation is discussed.

The last section briefly discusses some of the newer heterocyclic materials in which the volatile problem has been minimized or eliminated.

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1. POLYIMIDES COMPARED TO OTHER ADHESIVES

PI Adhesives are admirably suited for applications requiring long time exposure to temperatures in the 400 to 600°F. range and short time exposure to temperatures up to 1,000°F. They are, however, high priced adhesives and difficult and expensive to process. For this reason they should not be used in applications where epoxy or epoxy-phenolic adhesives would give satisfactory service.

Figure 1 depicts the high temperature strength of typical epoxy, epoxy-phenolic, polybenzimidazole (PBI) and PI adhesives. It can be seen that epoxies are available which show excellent strength retention up to 400°F. and modest strength retention at 600°F. The other three types of adhesives all exhibit excellent strength retention up to 600°F. and moderate strength at 1,000°F.

Where long time aging is required, epoxies and epoxy-phenolics are generally limited to applications requiring continuous service at temperatures no higher than 350°F. As shown by Figure 2, epoxy adhesives are available which will withstand 30,000 hours exposure at 350°F. Epoxy-phenolics have lower oxidative stability and show a significant drop in strength after 6,000 hours at 350°F. It should be noted that the above data applies to bonded aluminum. When the metal substrate is steel or titanium, oxidative degradation of the adhesives proceeds at a much more rapid rate and service life may only be 20% or less than that of bonded aluminum assemblies. For this reason, when long service life is required on steel or titanium substrates, it may be prudent to specify PI adhesives for applications involving continuous exposure at temperatures as low as 300°F.

The effect of metal substrates on the life of an adhesive is shown in Figure 3. In this case the adhesive is an epoxy-phenolic and the aging temperature is 500°F. It will be noted that time to zero strength is 500 hours on aluminum but is only 100 hours on a steel substrate. The fact that there is little loss of strength after 500 hours on steel aged in a nitrogen atmosphere indicates that the steel catalytically promotes oxidative degradation of the adhesives.

Figure 4 shows that when heat aging is carried out at 500°F., PI adhesives show excellent strength retention after 40,000 hours. The next best material (a PBI) shows good strength retention for only about 500 hours. At 600°F. (Figure 5) the PI shows good strength retention after 1,200 hours while the PBI shows little strength retention after only 100 hours.

Figure 6 briefly compares the cost and processing characteristics of the various adhesive types. The epoxies are easiest to process. They cure at moderate temperatures and pressure and, being free of volatiles, do not require a bleeder system. Their cost is also reasonably low. Epoxy-phenolics do release about 5% volatiles and bleeders and venting are frequently advisable. In other respects they are similar to the epoxies. Both PI and PBI adhesives require high temperature cures and have high volatile content. Elaborate bleeder systems and maintenance of a vacuum during the cure cycle is therefore required. In addition, material costs are high. Since the PBI adhesives are at least as difficult to process as PI adhesives and are inferior in heat stability, they are no longer widely used.

2. PROCESSING AND PERFORMANCE OF POLYIMIDES

PI adhesives are supplied in both liquid form and as a solid film. In addition, the adhesive may be filled or unfilled and may or may not contain an antioxidant. Aluminum powder filled adhesives are generally used for metal bonding applications while unfilled adhesives are used primarily for radome applications. Antioxidants are generally used in adhesives for bonding steel and titanium but are not required when bonding is to non-metallic substrates. Unless otherwise stated, the adhesive discussed in this section may be assumed to be a film type adhesive containing both aluminum powder and an arsenic type antioxidant.

2.1 EFFECT OF ANTIOXIDANT ON SERVICE LIFE

Figure 7 shows the effect that inclusion of an arsenic type antioxidant has on the strength retention of bonded titanium. With the antioxidant there is little loss of strength after 1,200 hours aging at 600°F. Without the antioxidant there is zero strength retention after 600 hours. Similar results are obtained on steel alloys. The reason for this phenomena is that both steel and titanium contain transition metals (iron in the case of steel and vanadium in the case of most titanium alloys). At high temperatures, in the presence of oxygen, these transition metals become oxidized. The transition metal oxides such as iron oxide and vanadium oxide are powerful pro-oxidants and cause catalytic decomposition of most organic materials. It has been postulated, but not to my knowledge proven, that the arsenic type antioxidant functions by inhibiting the formation of the transition metal oxides.

2.2 EFFECT OF CURE TEMPERATURE ON PROPERTIES

The high temperature strength developed by a PI adhesive is largely dependent on the temperature to which it was heated during processing. This is illustrated in Figure 8. It can be seen that a cure temperature of 350°F. results in an adhesive's having inadequate strength even at 350°F. When a post cure at 500°F. is employed, imidization is more complete and strength is respectable at temperatures up to 500°F. Where strength at extremely high temperatures is required, a post cure at 700°F. may be employed and gives about 1,000 psi lap shear strength at 1,000°F.

2.3 THE VOLATILE PROBLEM

The volatiles released during the cure of a PI adhesive come from two sources. First, water released as a result of the condensation reaction, and second, volatilization of retained solvent. A simplified representation of the reaction sequence which occurs during the cure of a PI adhesive is given in Figure 9. The prepolymer is formed by reacting a diamine with a dianhydride. This reaction is carried out in solution and the prepolymer is supplied by the resin manufacturer as a high solids solution. The adhesive manufacturer then incorporates the desired additives and, after coating the film on release paper, "B" stages the film to the desired degree. Since even very low molecular weight prepolymers are high melting and friable, some solvent is left in the adhesive film as a plasticizer. This retained solvent imparts drape and the desired degree of tack to the adhesive.

2.3 During bonding of the adhesive film, imidization occurs. Water is released as a result of this condensation reaction as well as the retained. solvent. If this solvent is not released soon enough in the bond cycle, imidization occurs prematurely and the resin becomes insoluble and precipitates in the solvent. When the solvent is subsequently volatilized later in the bond cycle, a weak, porous bond results because the resin is incapable of flow and as a result densification does not occur.

2.4 PROCESSING TO MINIMIZE VOLATILE PROBLEMS

The solvent most commonly used in PI adhesives is N-methyl-2-pyrrolidone (NMP) which boils at about 400°F. at atmospheric pressure. Since considerable imidization occurs long before the adhesive reaches even 350°F., this means precipitation would occur if processing were carried out at atmospheric pressure. Release of solvent earlier in the bond cycle is achieved through the use of vacuum. Figure 10 shows the boiling point of NMP at various degrees of vacuum. At about 13 psi vacuum the boiling point is depressed to about 280°F. With a 13 psi vacuum and a reasonably rapid heat-up rate of 3°F. per minute or faster, volatile release occurs soon enough in the bond cycle to minimize precipitation.

A typical cure cycle which has given good quality is shown in Figure 11. Bonding is carried out in an autoclave with a vacuum of 12 to 15 psi. To ensure proper mating of details 50 psi air pressure is applied to the other side of the vacuum bag. Time to heat the part to 350°F. is about one hour and it is held at 350°F. for one hour and cooled down to at least 150°F. before pressure is released and the part is removed from the autoclave. At this point the adhesive has cured enough so that it has enough strength to permit handling the part. The bonded part is then put into an oven at 350°F. and the oven temperature is gradually raised to 550°F. After a two hour hold at 550°F. imidization is essentially completed.

Figure 12 graphically illustrates the release of volatiles during the above cure cycle. Observations made in the laboratory indicate that the adhesive retains solubility and ability to flow and densify until the temperature reaches about 300°F. At this point the major portion of the pyrrolidone has evaporated and danger of precipitation has passed. The last 5% of weight loss is mainly water released during the condensation reaction.

Based on the previous discussion, it would appear to be quite simple to obtain good bonds if one only follows directions. This is largely true when small area bonds (such as 1/2 inch overlaps) are involved. However, when large area bonds are involved, volatile release is made much more difficult. In these cases venting and bleeder systems consisting of several layers of coarse weave glass cloth must be employed. Figure 13 shows the effect of bond area on the quality of the bond obtained. With a 1/2 inch wide bond area, about 3,500 psi lap shear is obtained. This progressively drops as the bond area increases to about only 500 psi for a 6 inch wide bond area. The quality of the bond may be improved by venting. In this case 1/16 inch diameter vent holes were bored in one of the skins. When the holes were spaced one inch apart, about 2,700 psi lap shear resulted. With two inch spacing lap shear strength was about 1,800 psi. Once venting was employed it will be noted that bond strength was largely independent of the width of the bond area. It should be noted that in this experiment, six plies of coarse glass fabric was employed as a bleeder to facilitate volatile release.

2.4 Similar problems exist in making large area sandwich bonds. Where perforated metal is employed as skins in the so called quiet nacelles used for noise abatement on jet engines, the volatile problem is not particularly serious. However, when the metal skins are not perforated, dealing with the volatile problem is more difficult. If perforated metal honeycomb core can be tolerated in the part, volatile problems are minimized.

Another approach is to carry out the bonding operation in two stages, first bonding one skin to one face of the core and completely curing the adhesive before bonding on the other face. A third technique is to prime the skins with liquid adhesive and apply a bead of liquid adhesive to the cell edges of the honeycomb. The adhesive may then be partially imidized by heating the skins and core to about 410°F. This leaves only about 1% solvent in the adhesive. Volatiles released during bonding may then be reduced by using a thinner than normal layer of adhesive film.

Combinations of the above techniques are synergistic in improving bond quality.

3. NEWER HETEROCYCLIC ADHESIVES

Recent research on high temperature adhesives has been primarily directed towards the development of heterocyclic compounds which do not release volatiles during cure. The two major classes of materials are, first, the thermoplastic heterocyclic compounds such as the polyphenylquinoxiline (PPQ resins) and thermoplastic PI's and, second, the addition reaction polyimides. The PPQ resins are extremely expensive at present and for this reason seem unlikely to be commercialized in the near future.

Thermoplastic PI resins are designed to remain soluble even after they have been fully imidized. Conventional PI resins become insoluble after imidization mainly because of side reactions which cause crosslinking. In the case of the thermoplastic PI resins these crosslinking reactions have been largely eliminated and the polymer remains linear and soluble after imidization.

Since the thermoplastic PI's are fully imidized they do not undergo further advancement during cure. As a result their softening point must be well above their anticipated service temperature. In practice a thermoplastic PI with a service temperature limit of 600°F. must be heated to about 750°F. under pressure to obtain flow and wetting of the metal substrate.

Few production autoclaves are capable of operating at these temperatures and the aerospace industry has shown no inclination of being willing to make a capital investment of the magnitude required to process these materials.

The thermoplastic PI's have one further disadvantage; being high melting materials, they make rigid films. As a result they lack drape and tack and will not conform to curved surfaces. Despite these faults, their freedom from volatiles will undoubtedly lead to their acceptance in many applications.

3. A second type of volatile free heterocyclic is the addition reaction PI resin. These are soluble, fully imidized PI's of relatively low molecular weight. Chain extension to a higher molecular weight is achieved via an addition reaction. The addition reaction introduces linkages having lower thermal stability than the imide linkages. As a result, these materials are limited to applications involving long time aging at temperatures no higher than about 400 or 450°F. In time, adhesives based on resins of this type should find use in applications where the service temperature is too high for epoxies but not high enough to require conventional PI adhesives.

FIGURE I

COMPARISON OF HIGH TEMPERATURE STRENGTH OF VARIOUS TYPES OF ADHESIVES

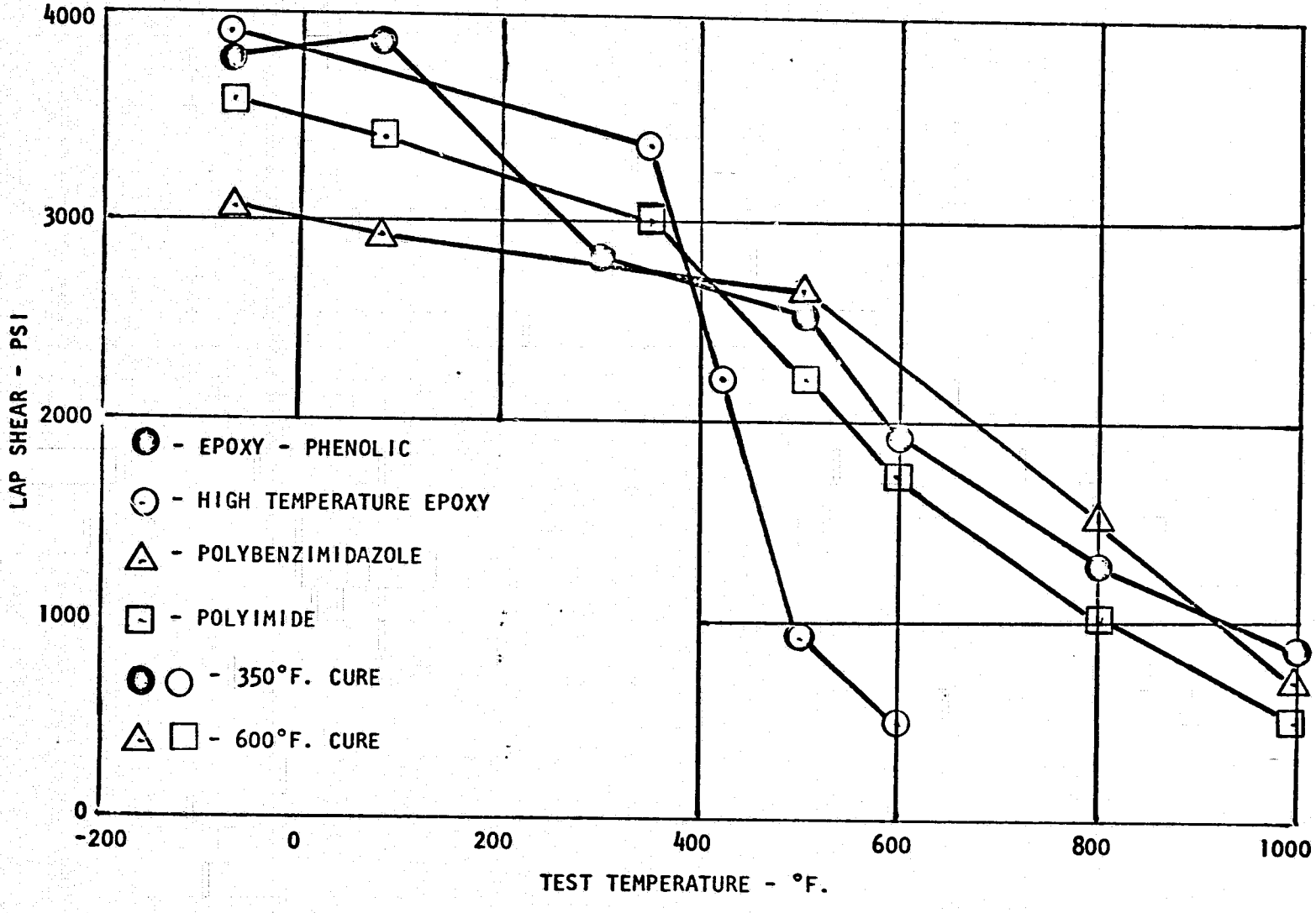


FIGURE 2

THERMAL STABILITY AT 350°F. OF EPOXY AND EPOXY-PHENOLIC ADHESIVES

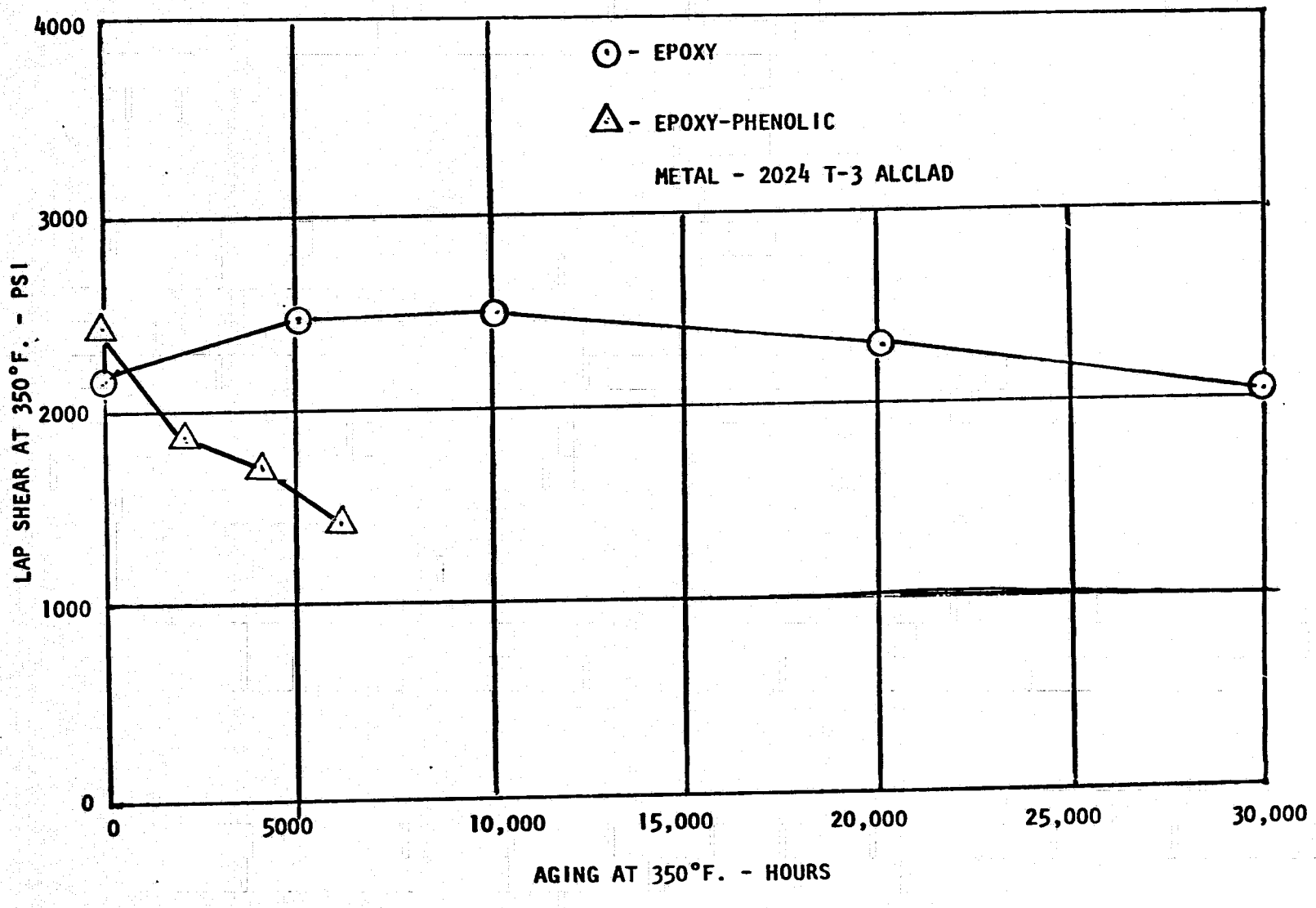


FIGURE 3

EFFECT OF SUBSTRATE AND ATMOSPHERE ON THERMAL STABILITY OF EPOXY-PHENOLIC ADHESIVE

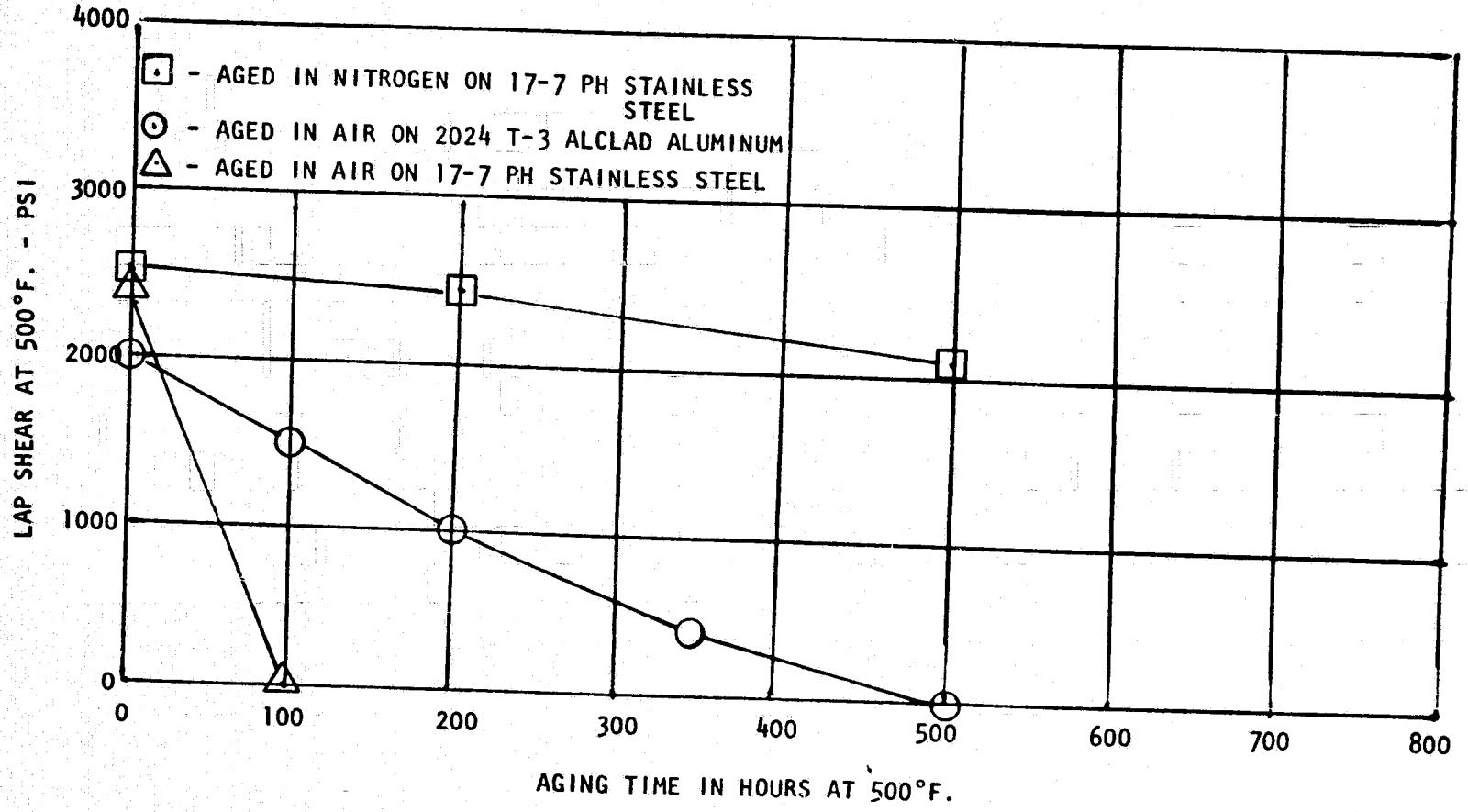


FIGURE 4

THERMAL STABILITY AT 500°F. OF VARIOUS ADHESIVES

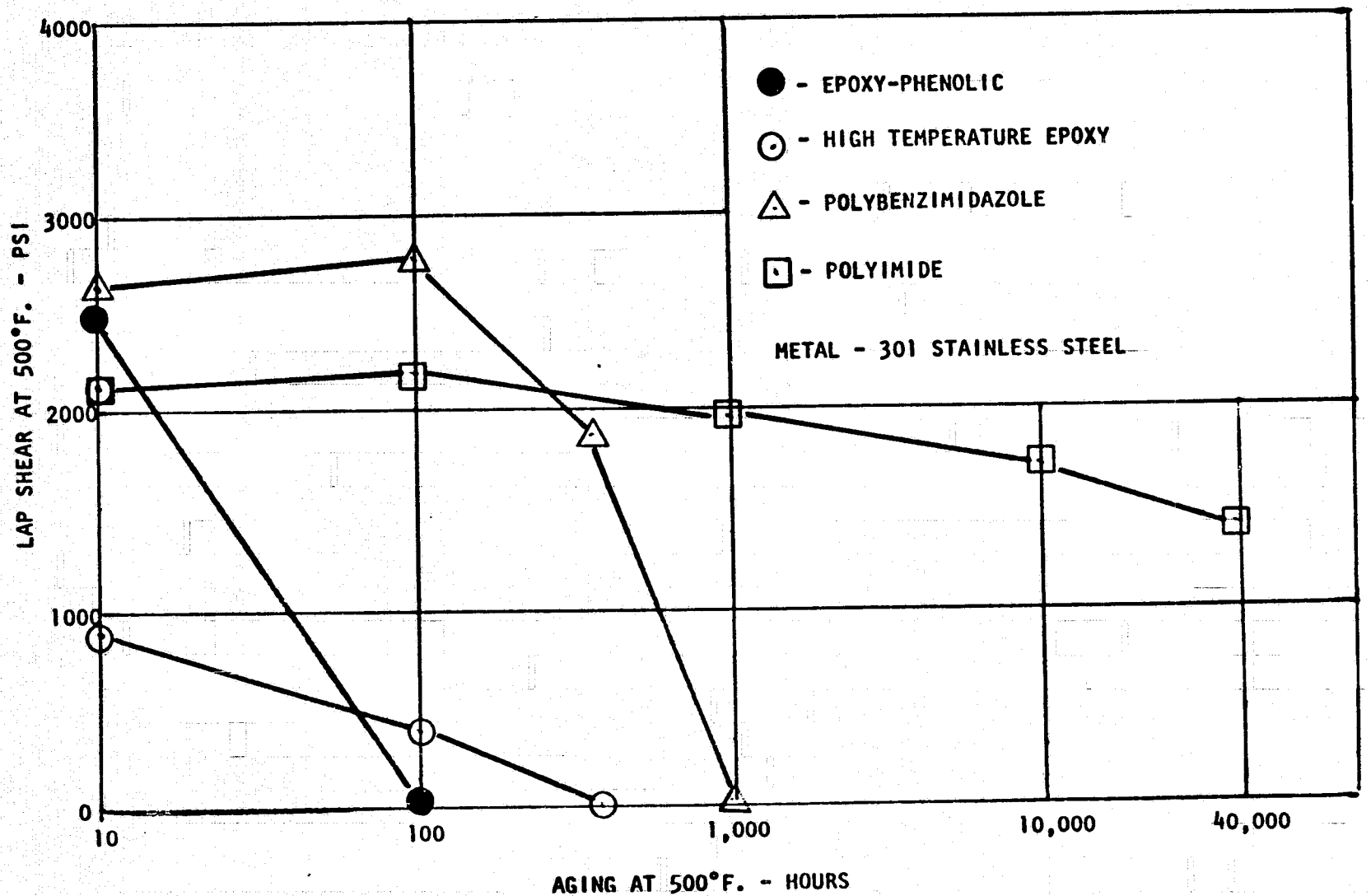


FIGURE 5

THERMAL STABILITY AT 600°F. OF VARIOUS ADHESIVES

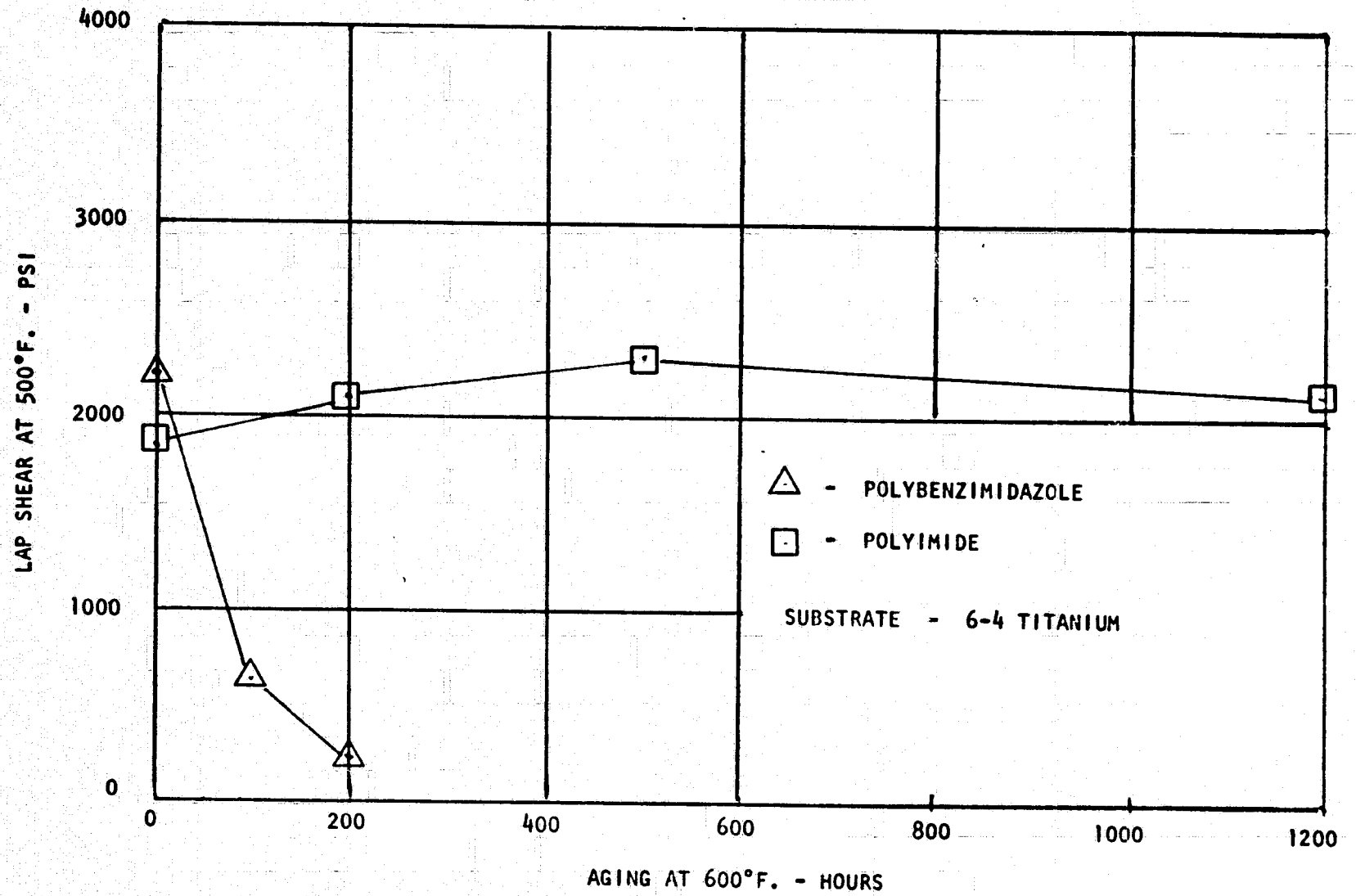


FIGURE 6

COST AND PROCESSING CHARACTERISTICS OF VARIOUS TYPES OF ADHESIVES

ADHESIVE TYPE	CURE TEMPERATURE	VOLATILES	MATERIAL COST	PROCESSING COST
EPOXY	350°F.	NONE	LOW	LOW
EPOXY-PHENOLIC	350°F.	5%	LOW	LOW TO MODERATE
POLYBENZIMIDAZOLE	500 - 700°F.	10 - 15%	HIGH	VERY HIGH
POLYIMIDE	500 - 700°F.	10 - 15%	HIGH	VERY HIGH

FIGURE 7

EFFECT OF ARSENIC ANTIOXIDANT ON THERMAL STABILITY OF POLYIMIDE ADHESIVE

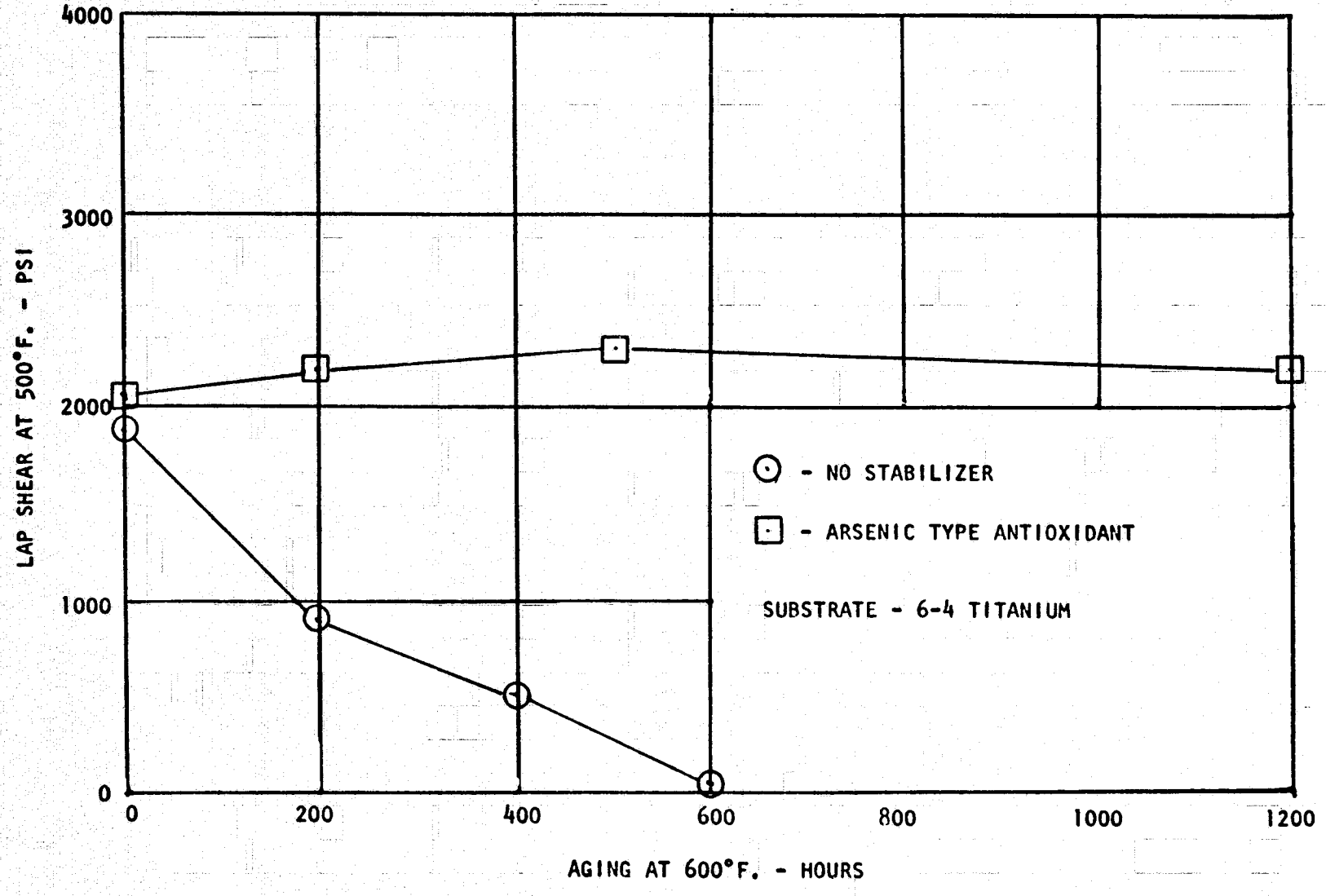


FIGURE 8

EFFECT OF CURE TEMPERATURE ON TENSILE SHEAR OF A POLYIMIDE ADHESIVE

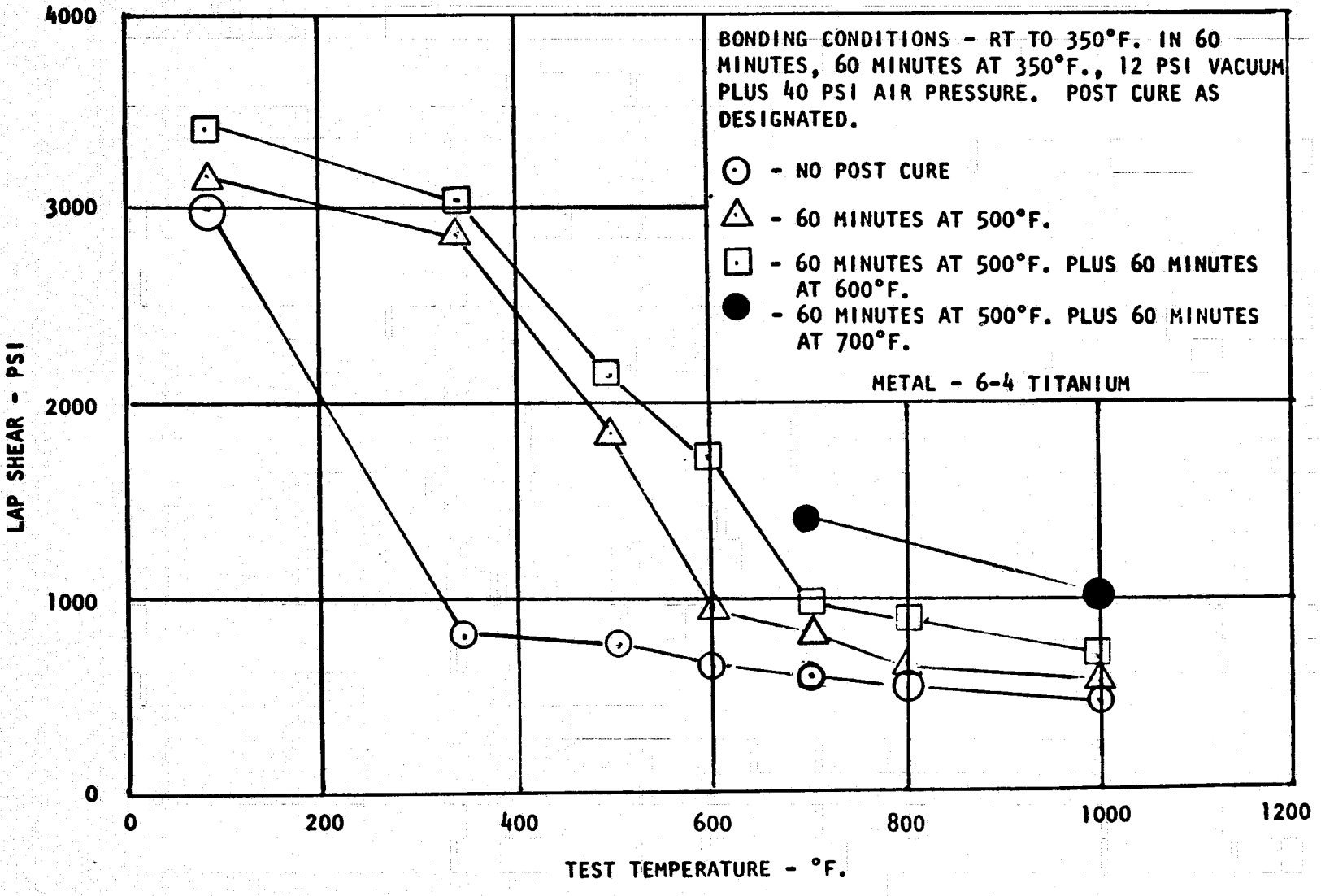
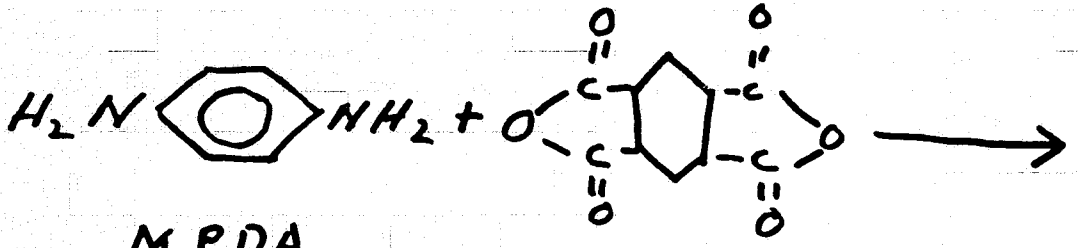
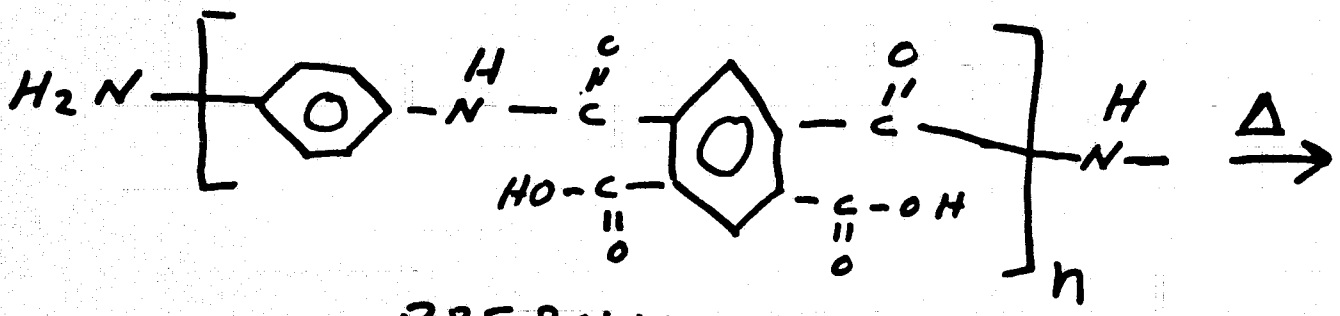


FIGURE 9

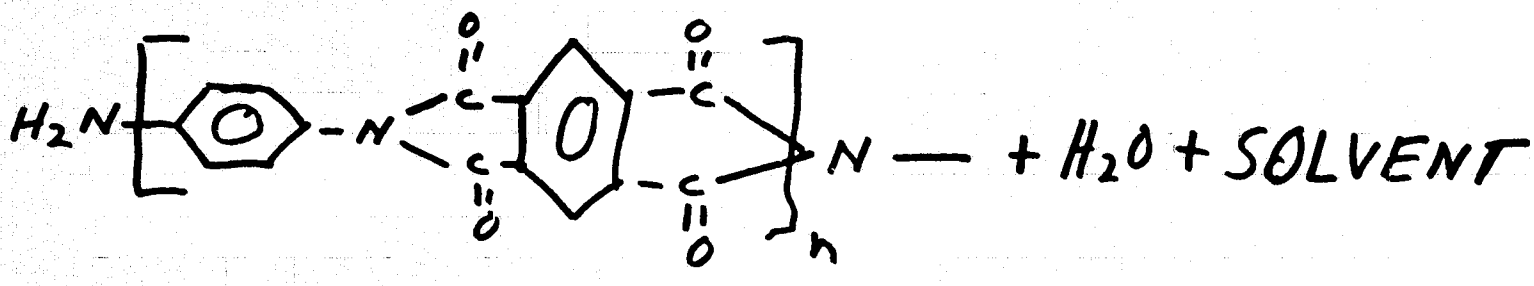
REACTION SEQUENCE FOR A PI RESIN



MPDA PMDA



PREPOLYMER



IMIDIZED RESIN

FIGURE 10

BOILING POINT CURVE OF N-METHYL-2-PYRROLIDONE

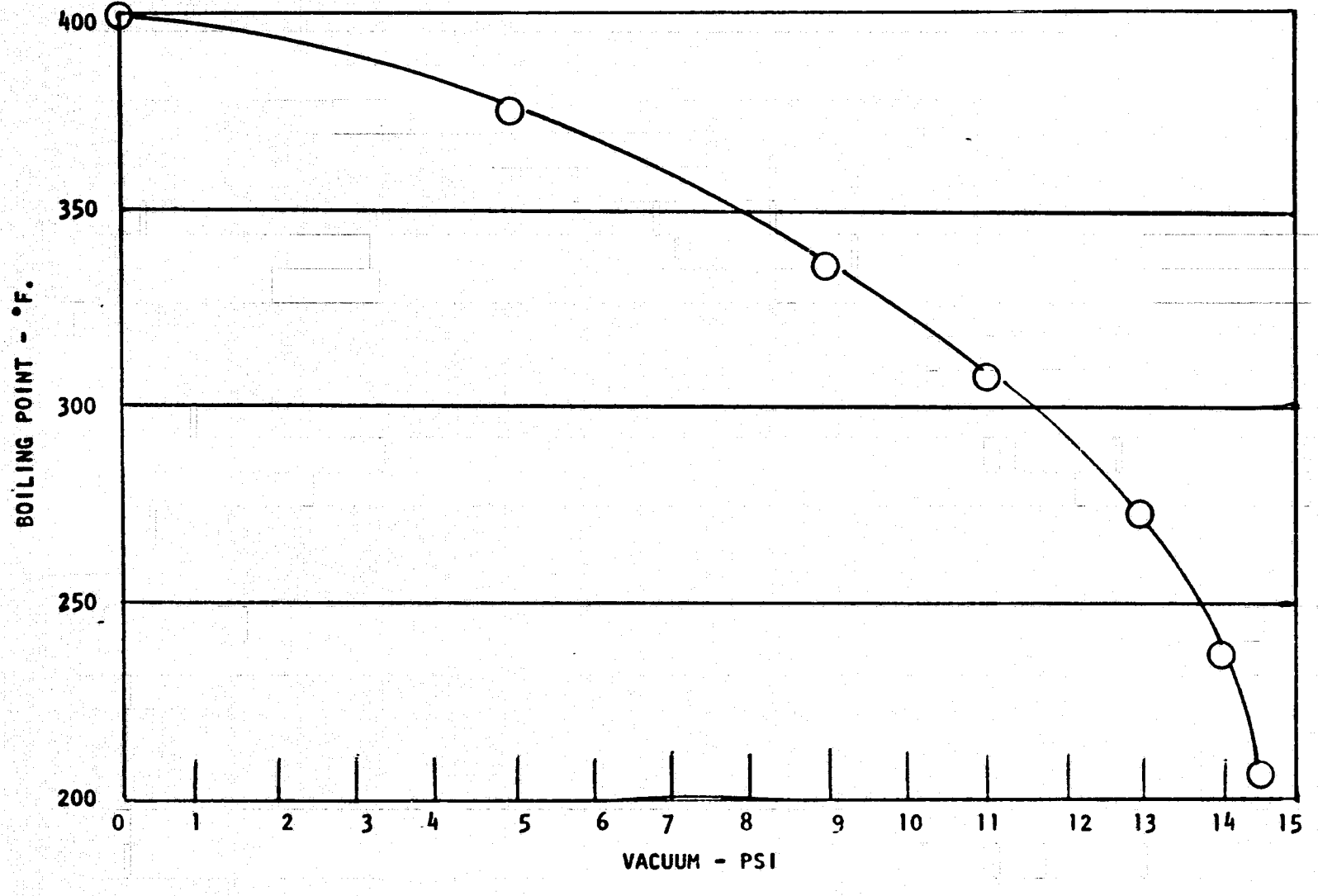


FIGURE 11

CURE CYCLE FOR POLYIMIDE ADHESIVE

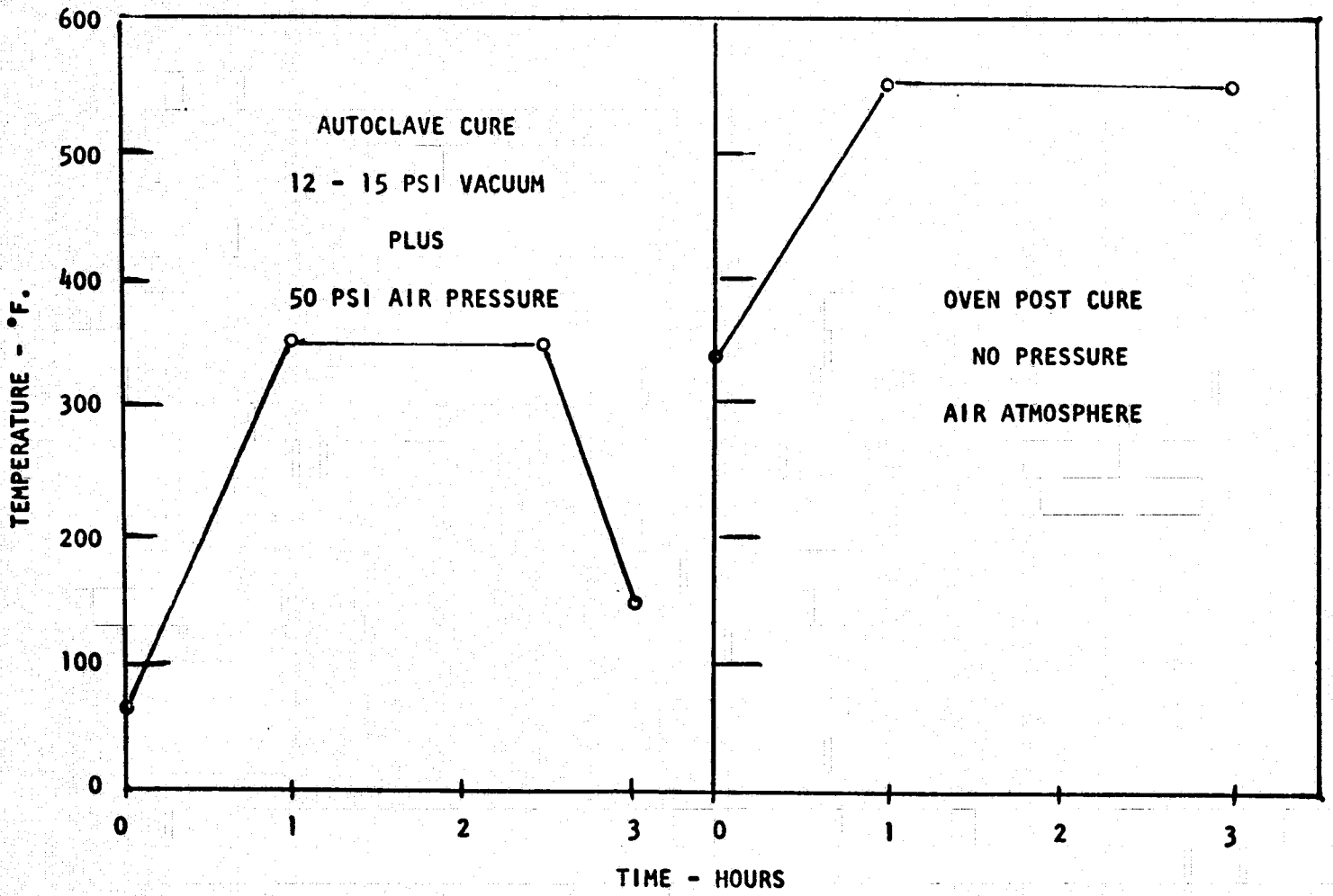


FIGURE 12

VOLATILE LOSS DURING CURE OF POLYIMIDE ADHESIVE

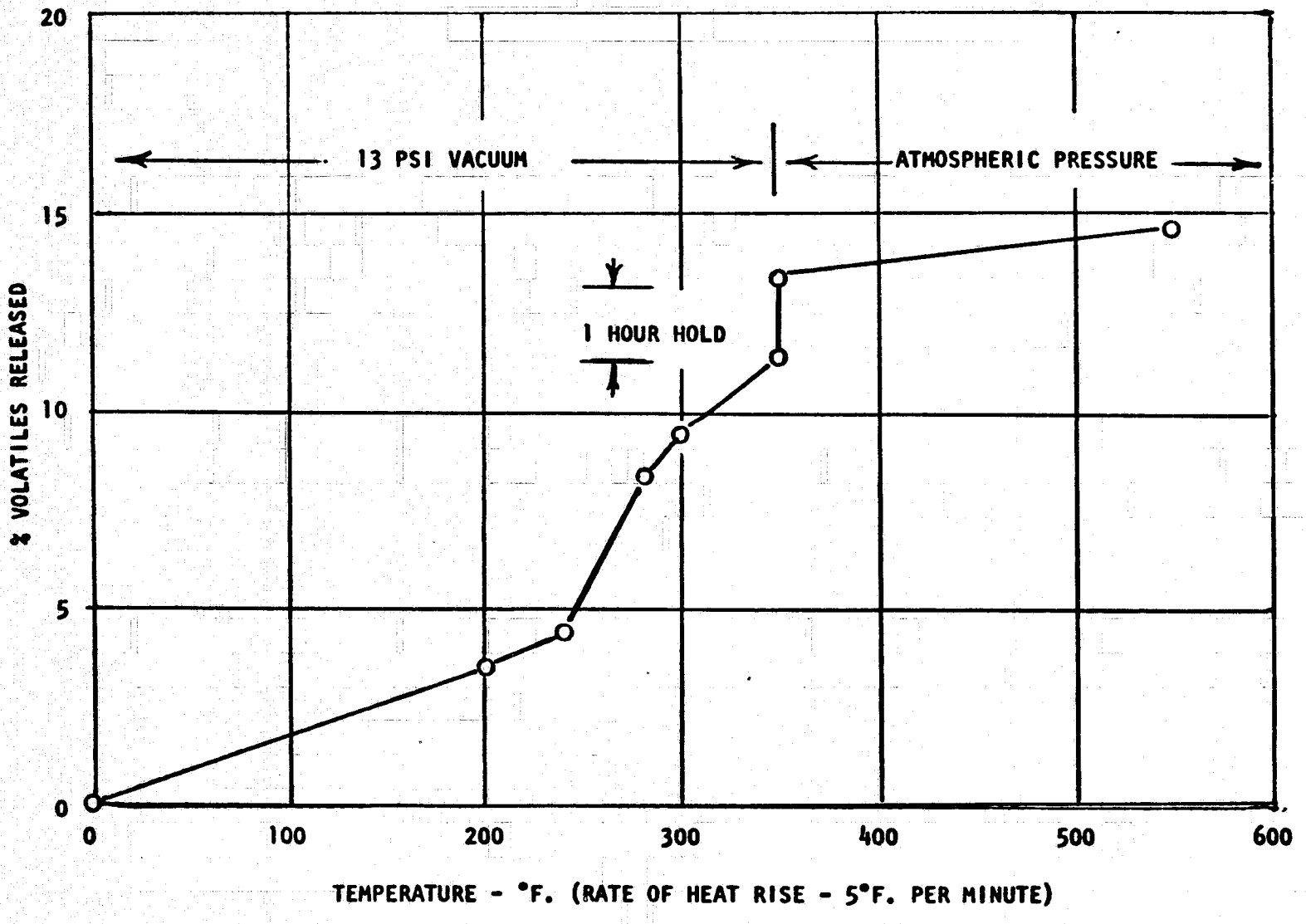
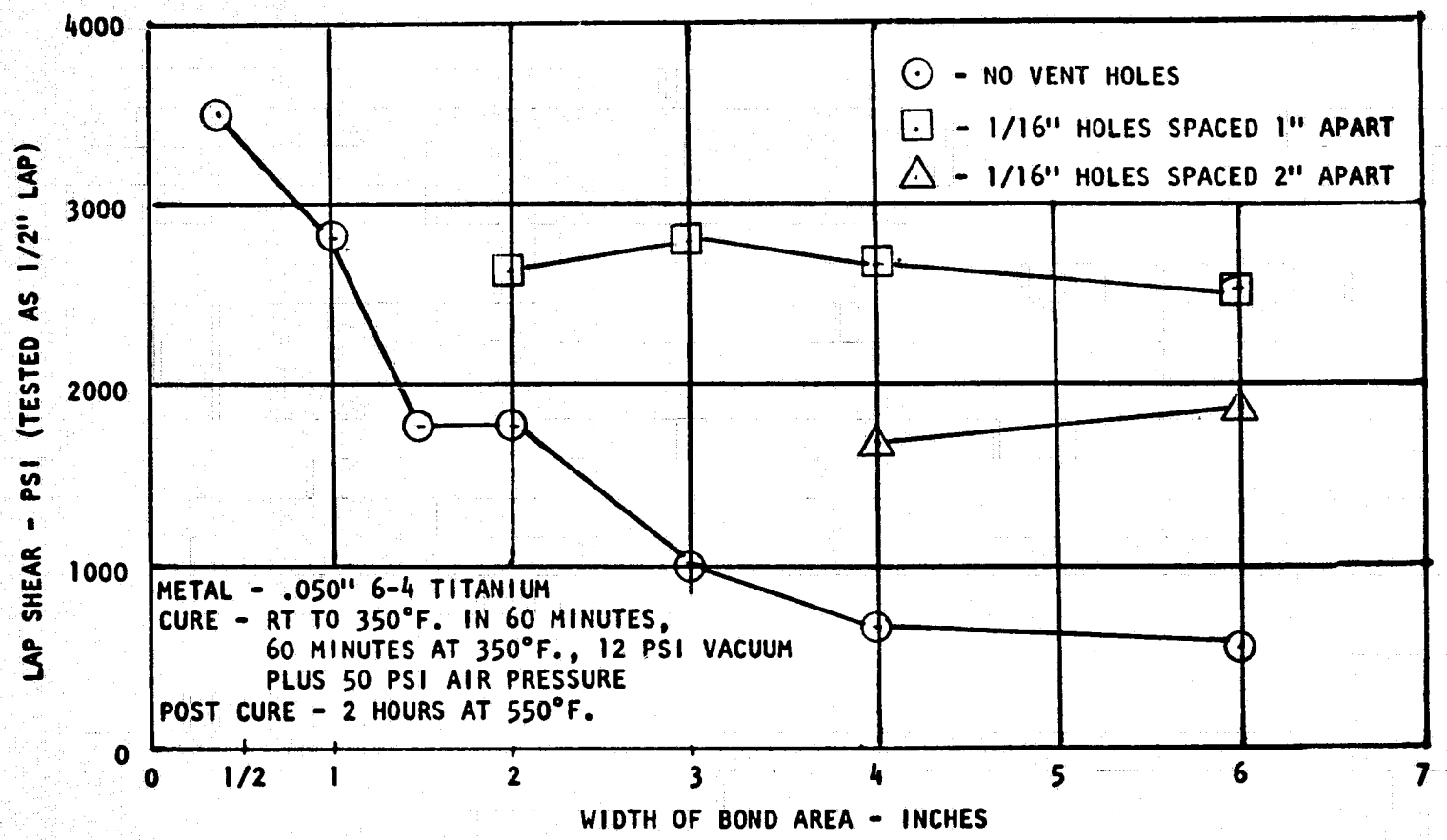


FIGURE 13

EFFECT OF VENT HOLES IN SKINS ON STRENGTH OF POLYIMIDE BONDS



PARTICIPANT COPIES OF SLIDES

PRESENTED AT NASA'S INDUSTRY

ASSESSMENT OF GRAPHITE-POLYIMIDE

COMPOSITE MATERIALS TECHNOLOGY

WILLIAMSBURG, VA. MARCH 17-19, 1975

CIBA-GEIGY CORPORATION
ARDSLEY, N.Y.

DR. S. S. HIRSCH

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THE GOAL

or

PRINCIPAL FEATURES OF WHAT WE UNDERSTAND THE INDUSTRY WANTS IN A POLYIMIDE MATRIX RESIN

- Autoclave processability at or below 400°F..
- Volatiles-free cure into void-free laminates.
- Reproducible processing into prime structure.
- Use of a low boiling, non-toxic, ecologically acceptable solvent.
- Freedom from solvent retention during processing.
- Storage-stable resin varnish and prepreg.
- Relatively low cost, simple system.
- Absolutely reliable quality and availability.
- Very epoxy-like (tough, tacky, etc.) except much less moisture sensitive.
- Long term serviceability to 600°F.

THE RESIN FAMILY

or

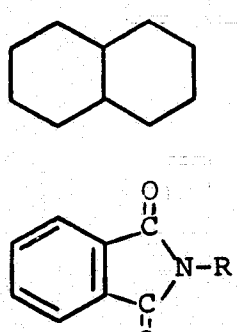
WHY THE ULTIMATE CANDIDATE

ALMOST CERTAINLY

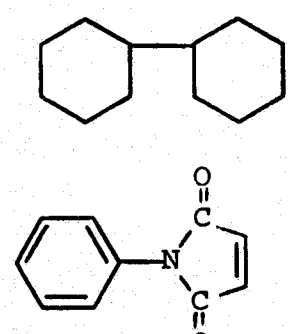
WILL BE

AN AROMATIC POLYIMIDE

Achieving long term thermal stability (especially in a processable system) at 600°F, appears to require the presence of fused rings.

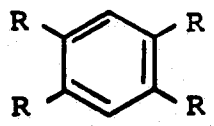


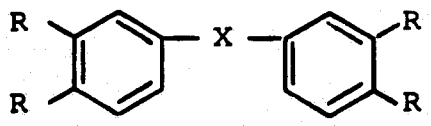
Fused rings



Non-fused rings

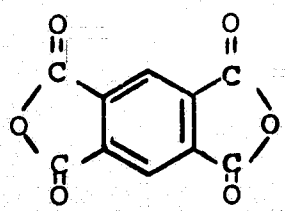
Fused rings are generated from tetrafunctional monomers.



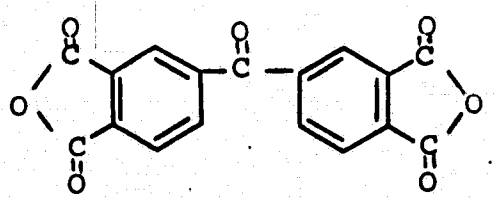


and

dianhydrides are the only inexpensive tetrafunctional monomers.



PMDA



BTDA

THERMAL PERFORMANCE

or

WHY I THINK 1000 HOUR + SERVICE AT 550-600°F MAY BE TOO AMBITIOUS A GOAL FOR COMMERCIAL PRODUCTION OF PRIME STRUCTURE POLYIMIDE PARTS OF COMPLEX SHAPE.

Three principal approaches:

1) Condensation Systems -

   Have 550-600°F long term service, process at 350°F, but eliminate volatiles.

2) Addition Cure Systems -

   Appear always to result in compromise of thermal properties.

3) Thermoplastic PI Candidates -

   Require exceptionally high processing temperatures.

PROPOSAL

or

MY CONTRIBUTION TO THIS SEMINAR

Don't try to squeeze the ultimate performance from the technology. The point of diminishing return is reached well before the ultimate performance limit.

Choose a design goal which seeks a balance between (idealized) maximum temperature performance and practically achievable processability of prime structure complex parts -

because -

willingness to design for (say) - 525°F long term, (600°F short term) performance almost certainly will permit achievement of facile and reproducible processing within the state - of - the - art of the 70's.

A KEY POINT OFTEN OVERLOOKED

or

THE IMPACT OF BUSINESS POTENTIAL ON THE INDUSTRY'S DEVELOPMENT EFFORT

Fact, or at least our conclusion:

The majority of commercial possibilities for thermoset resins with temperature capability higher than epoxies or phenolics lies in the range 400 - 525°F.

Industry will concentrate on developing candidates with greatest business potential. This will result in re-direction of effort which could be committed to processable candidates in the 525 - 600°F range.

This fact, coupled with the much greater difficulty of achieving a "highly processable" (See Chart I) candidate for fabrication into complex-shaped, prime structural parts for long term 550 - 600°F service can be expected to result in a paucity of new candidates.

KEY CIBA-GEIGY CANDIDATES

or

ON WHAT WE'RE BETTING

THE FUTURE

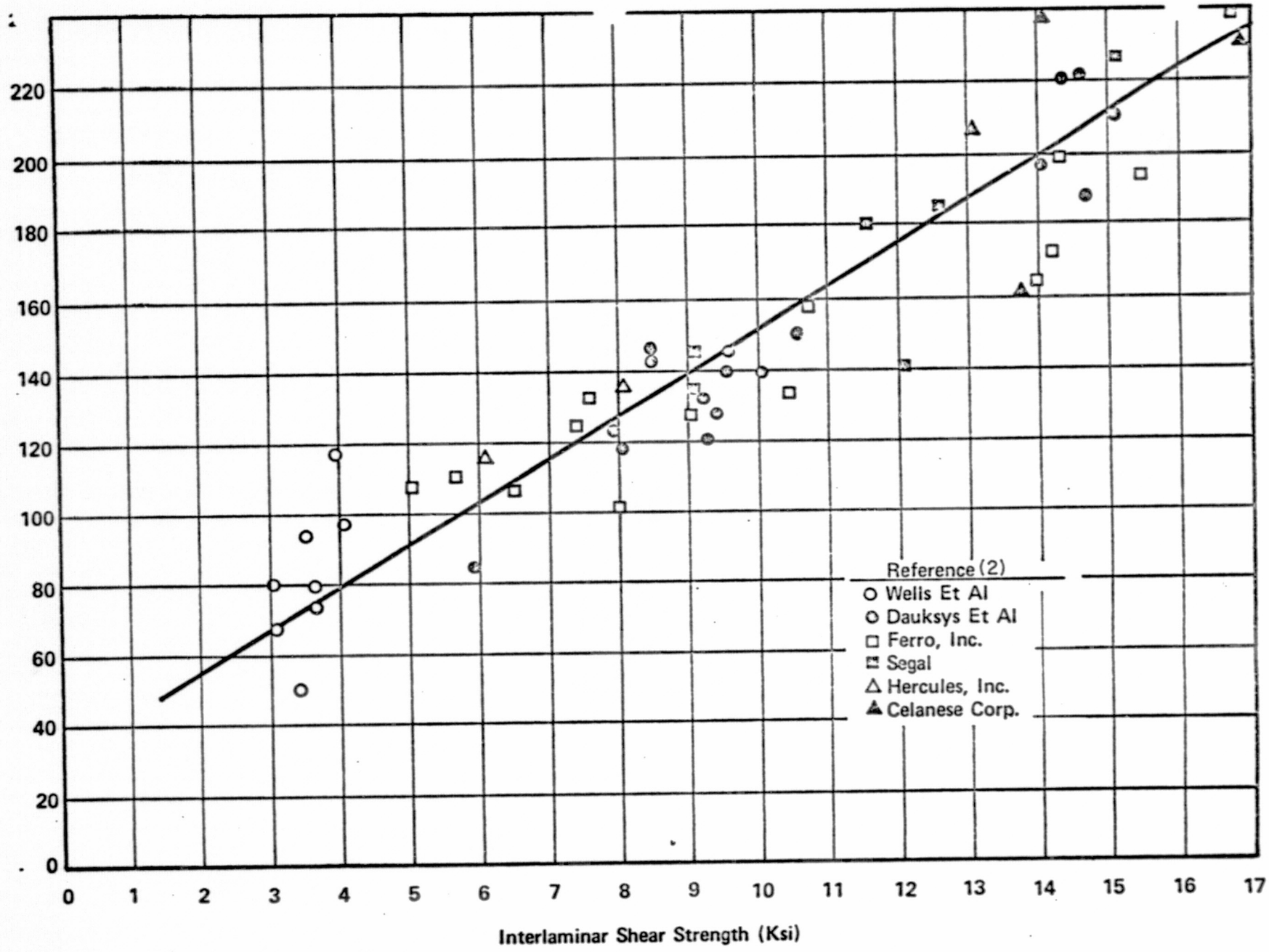
FOR HIGH TEMPERATURE RESINS

- A2 - Alternate (525°F long term service)
- Xylok (500°F long term service)
- NCNS resins (450°F *long term service)
- Much more I can't talk about yet, except to say the objective lies below 550 - 600°F long term service.

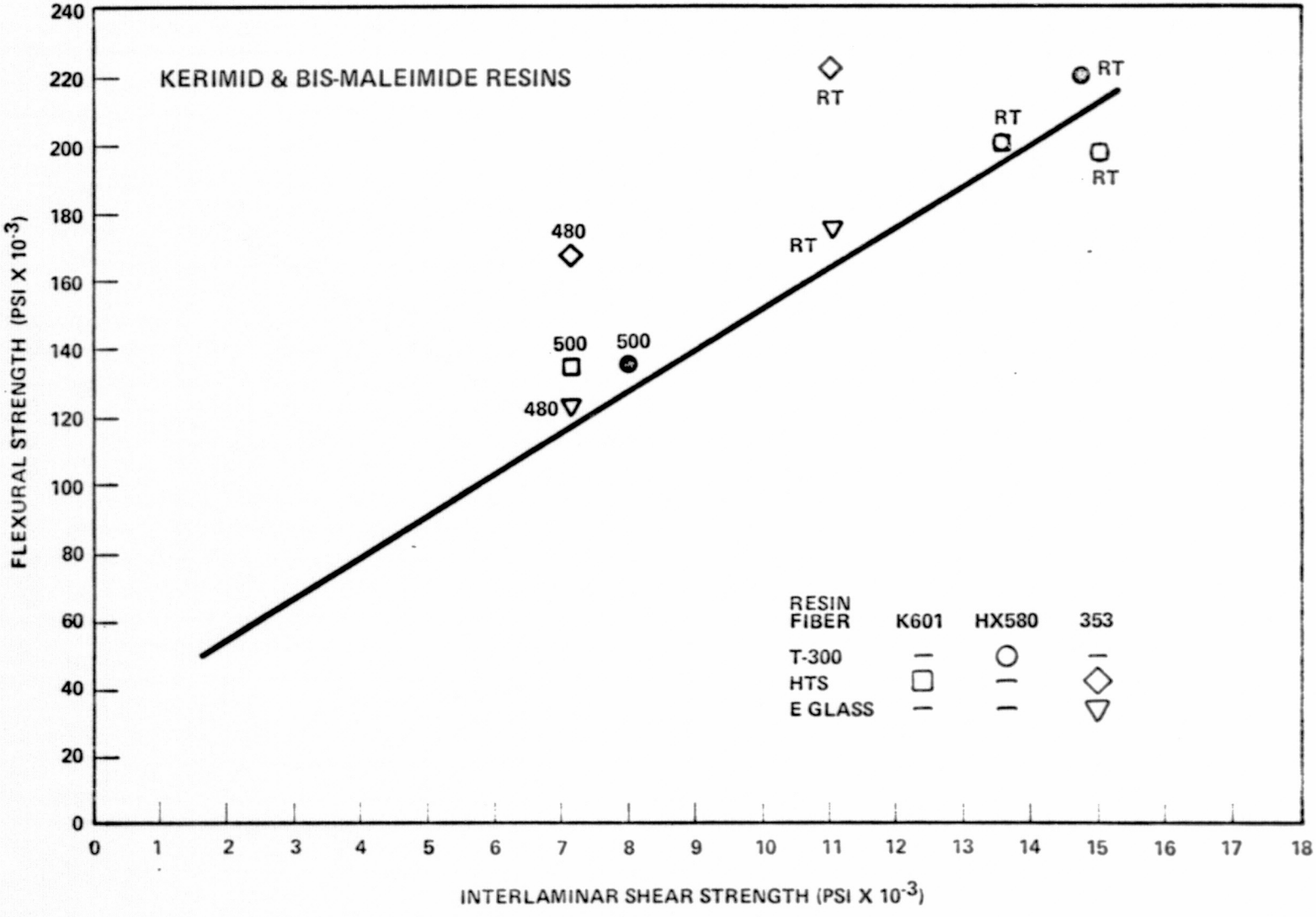
* Achievement of 475 - 500°F long term performance appears possible with additional development.

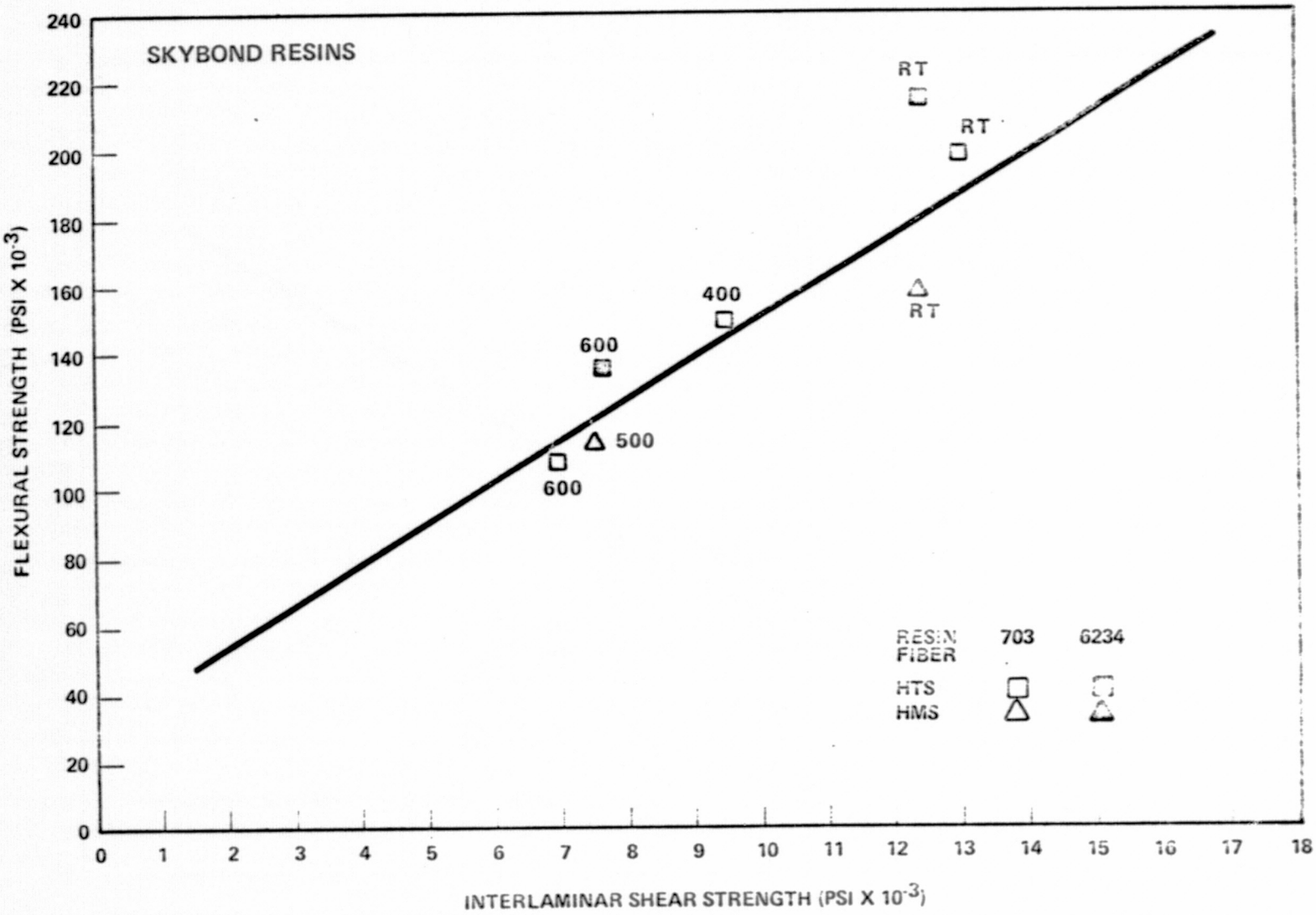


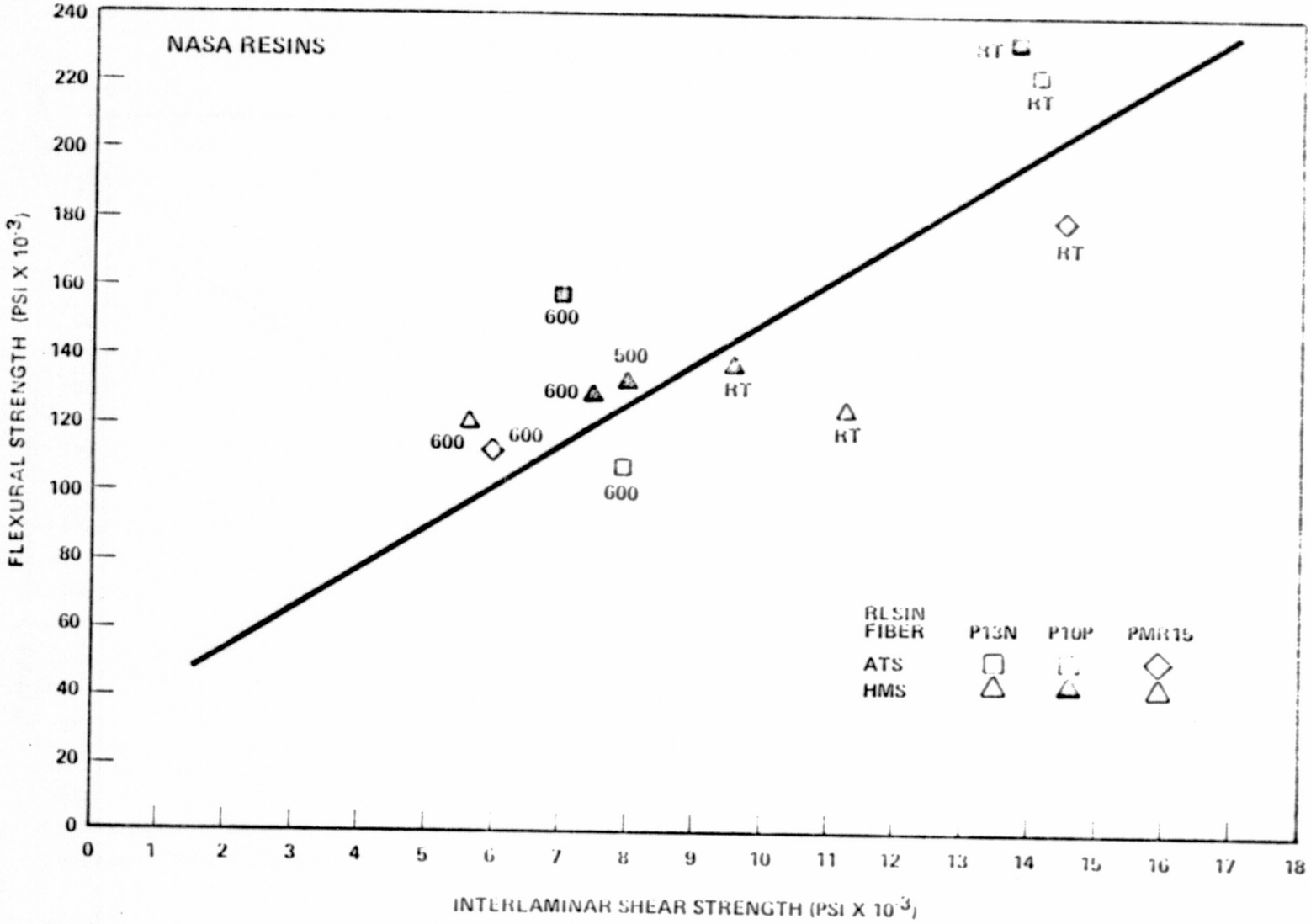
6342 NORTH IRWINDALE AVENUE
AZUSA, CALIFORNIA 91702

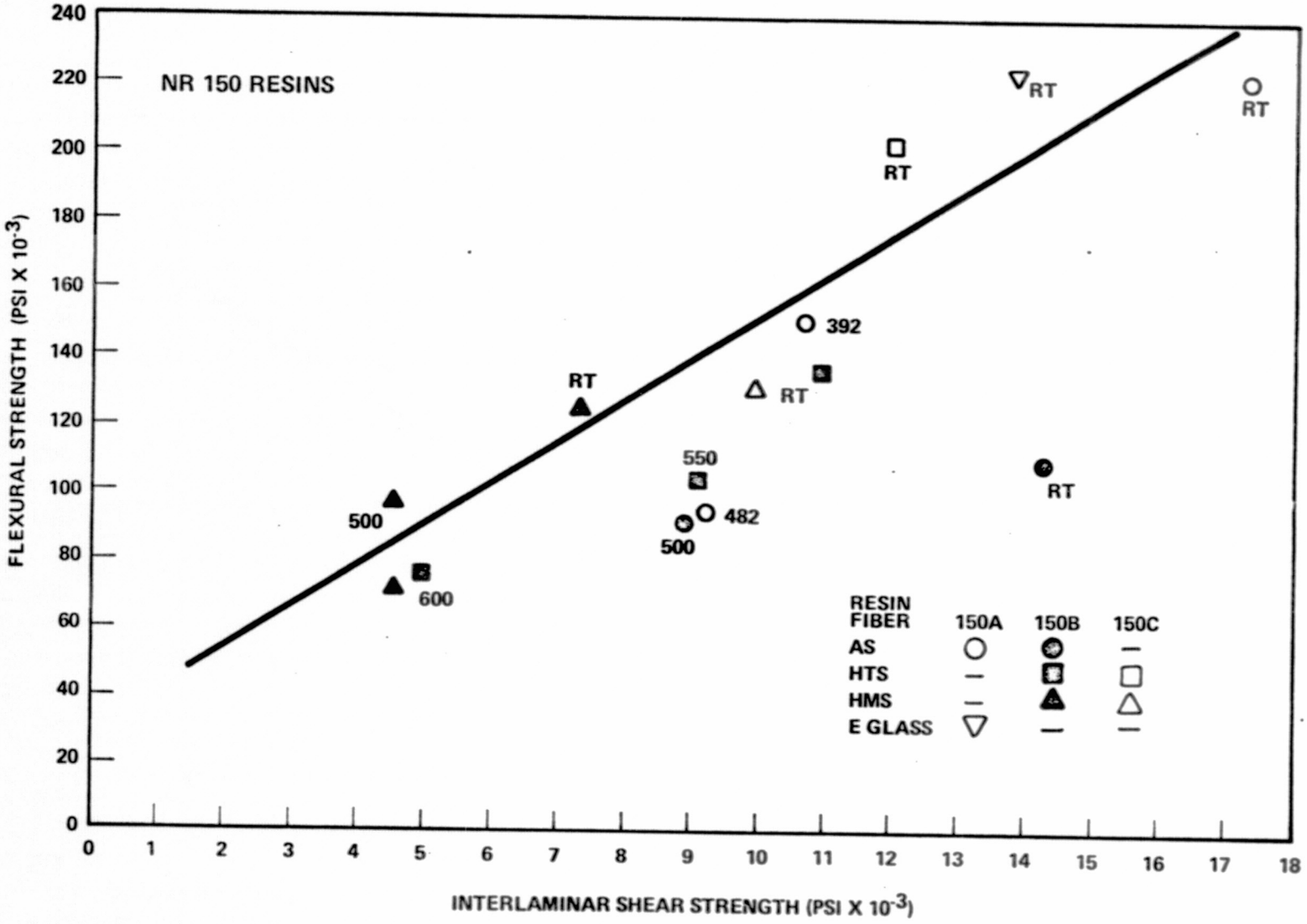


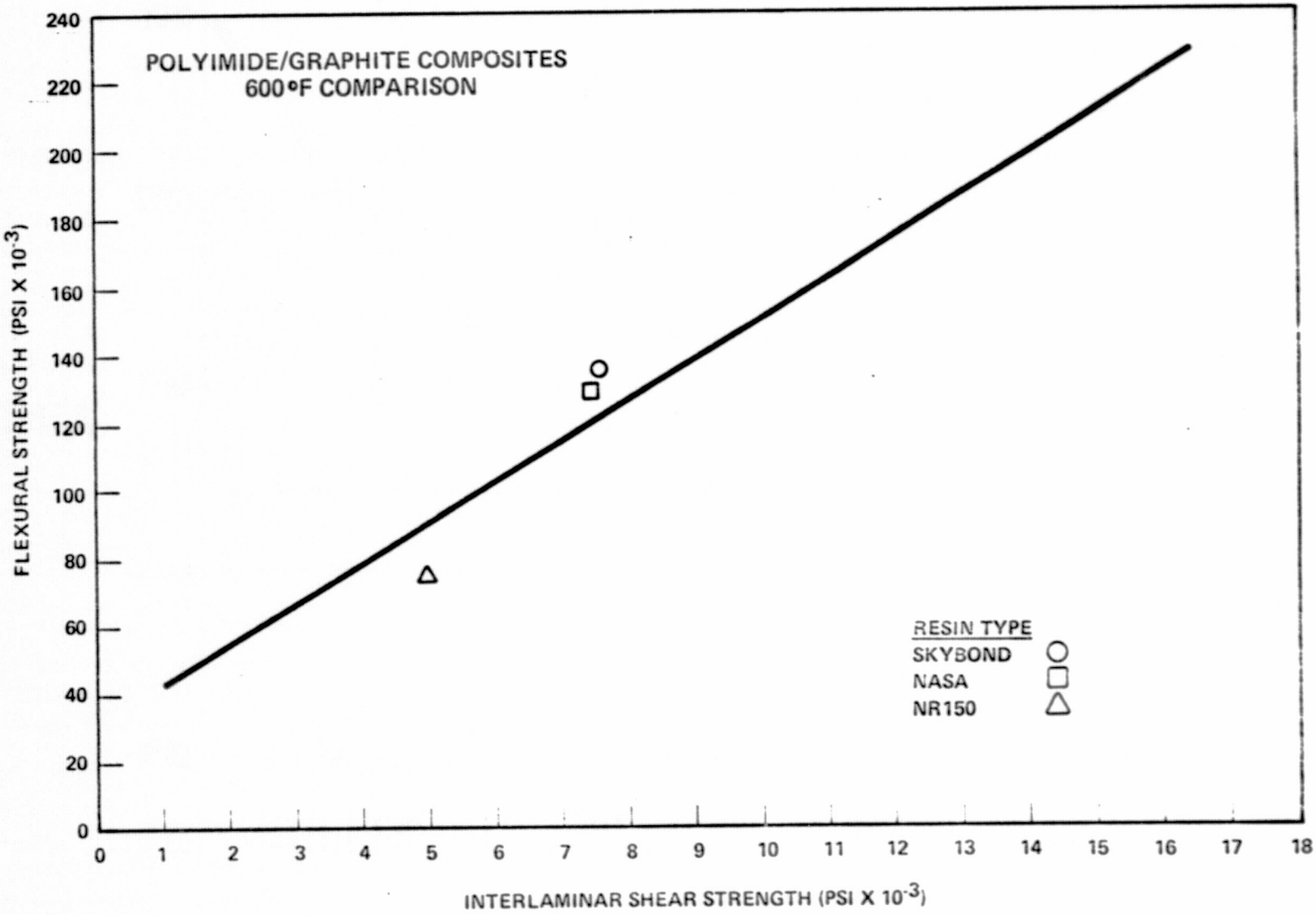
CORRELATION OF FLEXURAL STRENGTH AND INTERLAMINAR SHEAR STRENGTH FOR GRAPHITE/EPOXY COMPOSITES


KERIMID & BIS-MALEIMIDE RESINS
FLEXURAL STRENGTH (PSI X 10-3)
INTERLAMINAR SHEAR STRENGTH (PSI X 10-3)
RT
RT
RT
RT
RT
480
480
500
500
RESIN
FIBER
K601
HX580
353
T-300
HTS
E GLASS

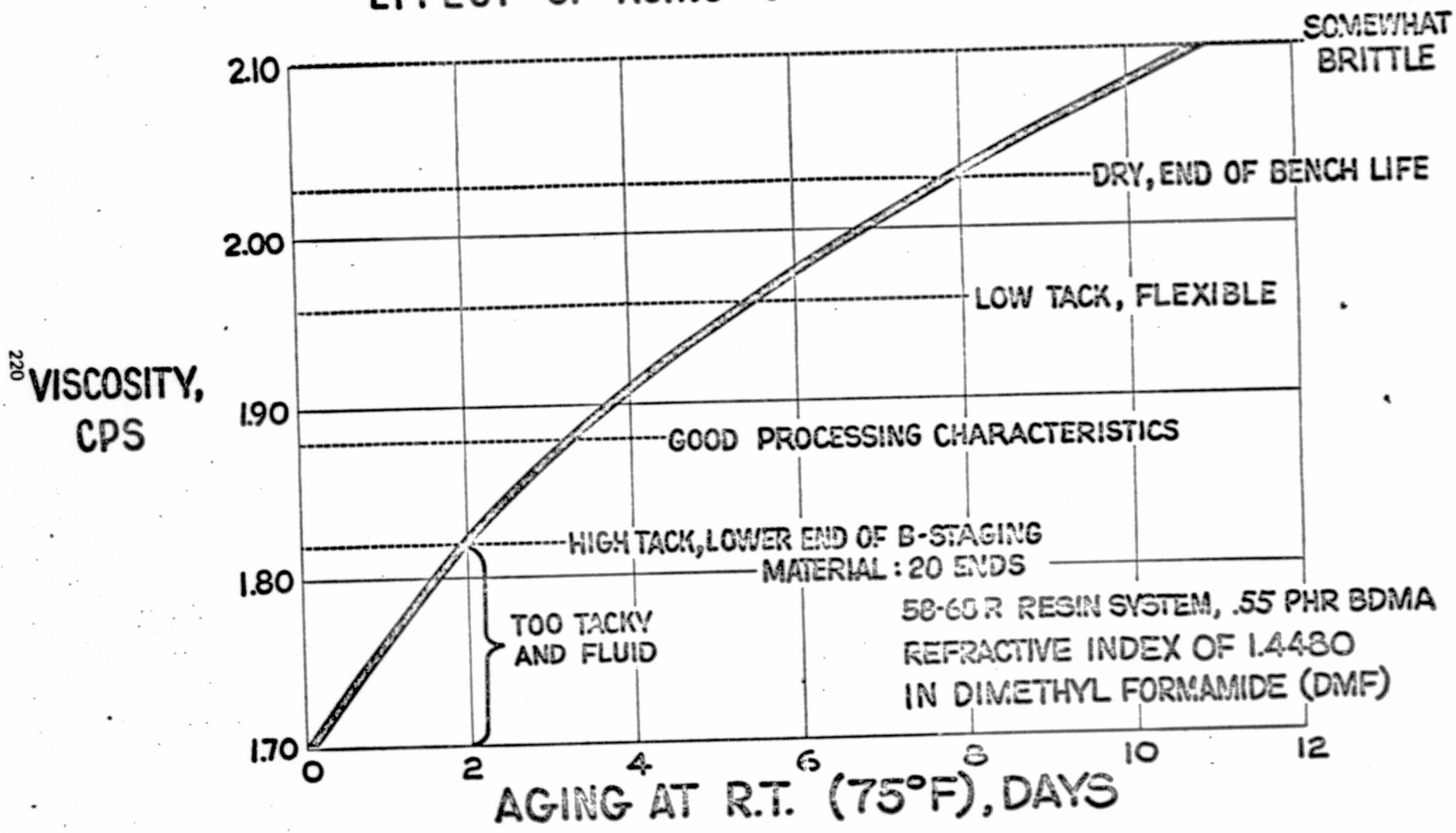

SKYBOND RESINS
RT
RT
RT
400
600
500
600
RESIN
FIBER
703
6234
HTS
HMS
FLEXURAL STRENGTH (PSI X 10-3)
INTERLAMINAR SHEAR STRENGTH (PSI X 10-3)
0
20
40
60
80
100
120
140
160
180
200
220
240
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

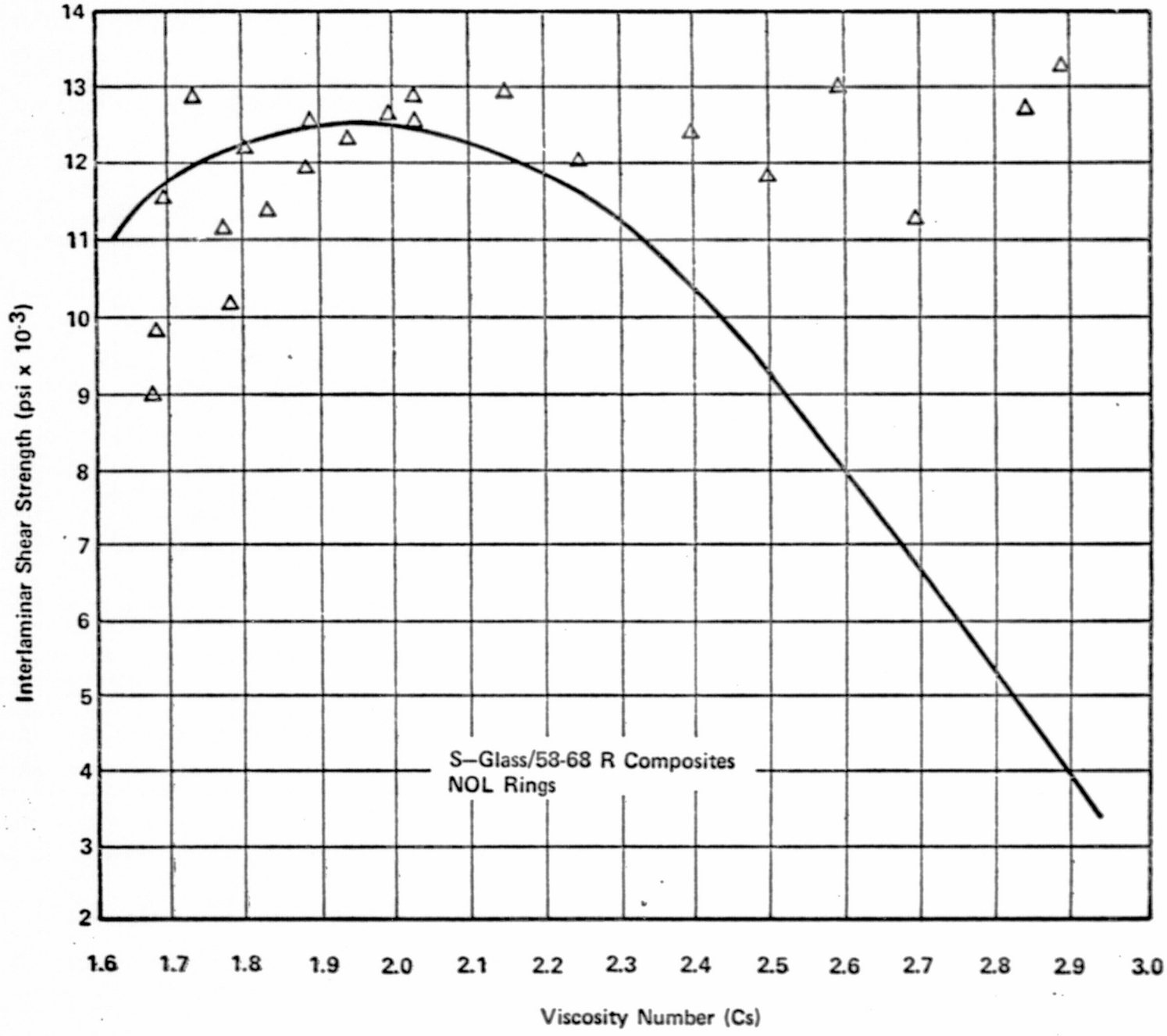

NASA RESINS
FLEXURAL STRENGTH (PSI X 10^{-3})
INTERLAMINAR SHEAR STRENGTH (PSI X 10^{-3})
RT
RT
RT
RT
RT
600
500
600
600
600
600
RESIN
FIBER
P13N
P10P
PMR15
ATS
HMS


NR 150 RESINS
FLEXURAL STRENGTH (PSI X 10-3)
INTERLAMINAR SHEAR STRENGTH (PSI X 10-3)
RT
RT
RT
RT
RT
392
550
482
500
500
600
RESIN
FIBER
150A
150B
150C
AS
HTS
HMS
E GLASS

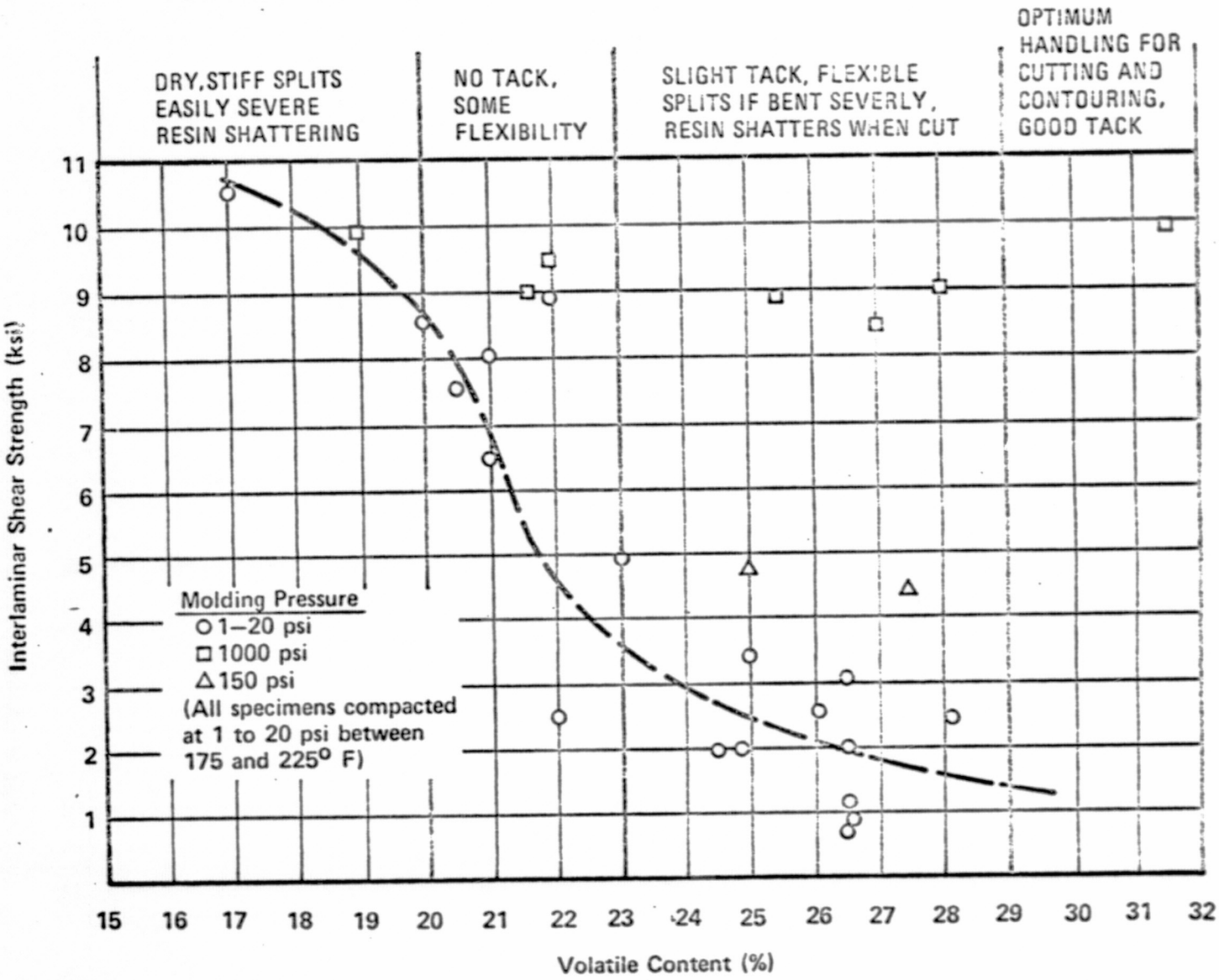

POLYIMIDE/GRAPHITE COMPOSITES
600°F COMPARISON
FLEXURAL STRENGTH (PSI X 10-3)
INTERLAMINAR SHEAR STRENGTH (PSI X 10-3)
RESIN TYPE
SKYBOND
NASA
NR150
0
20
40
60
80
100
120
140
160
180
200
220
240
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

EFFECT OF AGING ON VISCOSITY INDEX



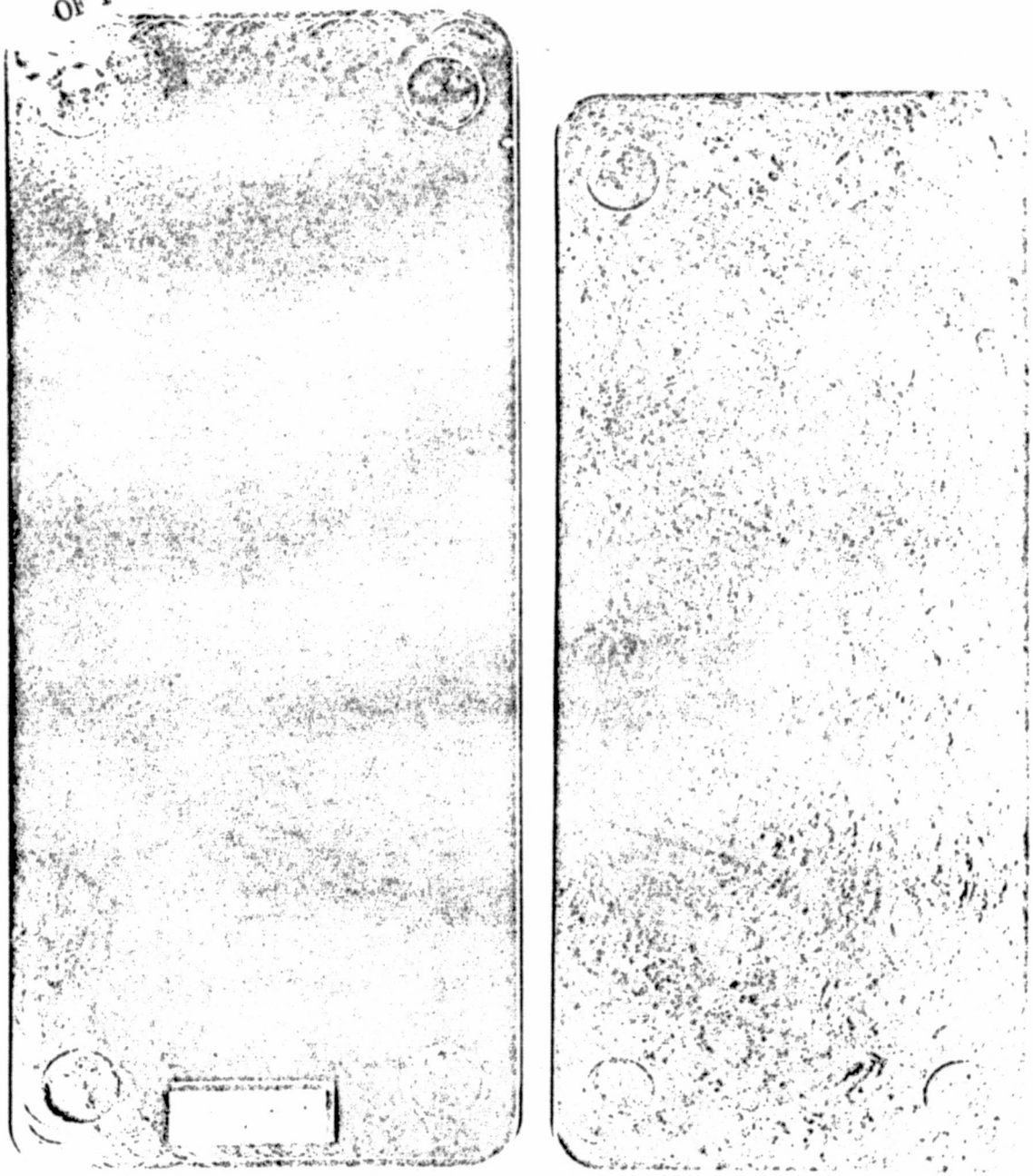


INFLUENCE OF HEAT DURING WINDING ON INTERLAMINAR SHEAR STRENGTH



EFFECT OF VOLATILES AND MOLDING PRESSURE ON INTERLAMINAR SHEAR STRENGTH, BORON/PI (SKYBOND 703) COMPOSITES.

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CLASSIFICATION OF COMPOSITE RESINS AS PREPREGS
ACCORDING TO PROCESSABILITY

CLASS I – TRACTABILITY WITHOUT SOLVENT

CLASS II – TRACTABILITY WITH SOLVENT

CLASS III – TRACTABILITY WITH SOLVENT AND VOLATILE
REACTION PRODUCTS

POLYIMIDE RESIN PROCESSABILITY

CLASS	RESIN	COMMENTS
I	NASA	IMMIDIZED, DRY, BOARDY
	K601, 353	DRY, BOARDY
	HX580	TACKY
	NR150's	AS THERMOPLASTIC, VERY STIFF
II	K601	TACKY
III	SKYBOND	TACKY TO DRY
	NASA	TACKY TO DRY
	NR150's	TACKY TO DRY

POLYIMIDE RESIN PROCESSABILITY

CLASS	RESIN	COMMENTS
I	NASA	IMMIDIZED, DRY, BOARDY
	K601, 353	DRY, BOARDY
	HX580	TACKY
	NR150's	AS THERMOPLASTIC, VERY STIFF
II	K601	TACKY
III	SKYBOND	TACKY TO DRY
	NASA	TACKY TO DRY
	NR150's	TACKY TO DRY

SUMMARY – BIS-MALEIMIDE RESINS

I. PERFORMANCE
   1. AT 500 °F - ALL MECHANICAL PROPERTIES AT LEAST 50% OF BEST R.T. EPOXIES.
   2. GREATER THAN 50% IN MODULUS AND UNI-TENSION

II. COST
   1. MAXIMUM PREMIUM OF 50% OVER EPOXIES
   2. MORE LIKELY 25%

III. ESTABLISHED MAXIMUM TEMPERATURE
   500 °F ? – 550 °F ? – ?

IV. OTHER
   1. FABRIC REINFORCEMENT

SUMMARY – BIS-MALEIMIDE RESINS

I. PERFORMANCE
   1. AT 500 °F - ALL MECHANICAL PROPERTIES AT LEAST 50% OF BEST R.T. EPOXIES.
   2. GREATER THAN 50% IN MODULUS AND UNI-TENSION

II. COST
   1. MAXIMUM PREMIUM OF 50% OVER EPOXIES
   2. MORE LIKELY 25%

III. ESTABLISHED MAXIMUM TEMPERATURE
   500 °F ? – 550 °F ? – ?

IV. OTHER
   1. FABRIC REINFORCEMENT

SUMMARY – SKYBOND RESINS

I. PERFORMANCE
   1. AT 600°F - ALL MECHANICAL PROPERTIES AT LEAST 50% OF BEST EPOXIES AT R.T.
   2. GREATER THAN 50% IN MODULUS AND UNI-TENSION

II. COST
   1. UNCLEAR DUE TO PRECISION REQUIRED IN PREPREG AND PROCESS
   2. EXPECT 100% PREMIUM OR MORE

III. QUESTION
   CAN SHRINKAGE BE TOLERATED ?

IV. OTHER
   1. HOW TO TEST THE PREPREG ?
   2. ENVIRONMENTAL CONTROLS ?

SUMMARY – NASA RESINS

I. PERFORMANCE
   1. AT 600°F - ALL MECHANICAL PROPERTIES AT LEAST 50% OF BEST EPOXIES AT R.T.
   2. GREATER THAN 50% IN MODULUS AND UNI-TENSION

II. COST
   1. MAXIMUM PREMIUM OF 100% OVER EPOXIES
   2. AS LITTLE AS 10% PREMIUM IF COMPRESSION MOLDED

III. QUESTIONS
   1. CAN PMR–TYPE BE AUTOCLAVE-MOLDED?
      a. VOID CONTENT – 1% ?
      b. REPRODUCIBILITY ?
   2. BESIDES TRADITIONAL AUTOCLAVES, CAN TOOLING AND EQUIPMENT BE CREATED TO ACHIEVE :
      a. REQUIRED HEAT FLUX
      b. REQUIRED PRESSURE

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VIEW-GRAPH PRESENTATION

BY

HUGH H. GIBBS

PLASTICS DEPARTMENT

E. I. DU PONT DE NEMOURS & CO., INC.

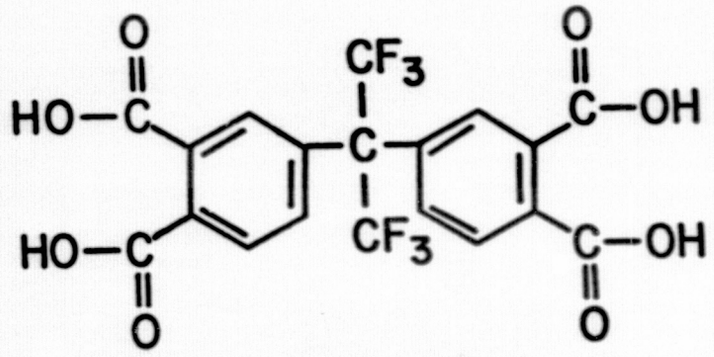
FOR

NASA-LANGLEY GRAPHITE-POLYIMIDE-
MATERIALS TECHNOLOGY MEETING

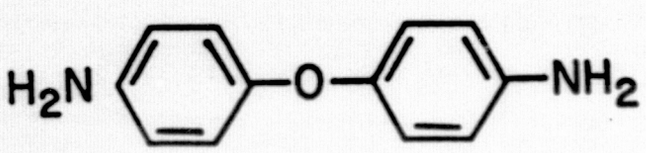
WILLIAMSBURG, VIRGINIA

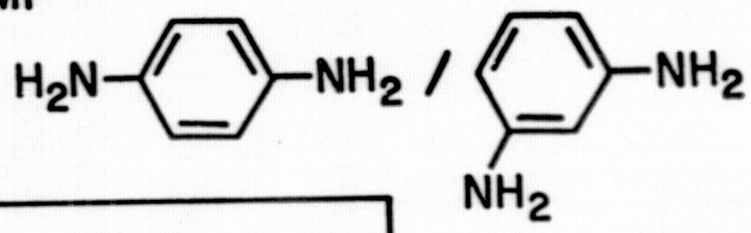
MARCH 17-19, 1975

NR-150 POLYIMIDE BINDER CHEMISTRY



NMP





NR-150A2

T_g = 280-300°C

536-572°F

NR-150B2

T_g = 350-371°C

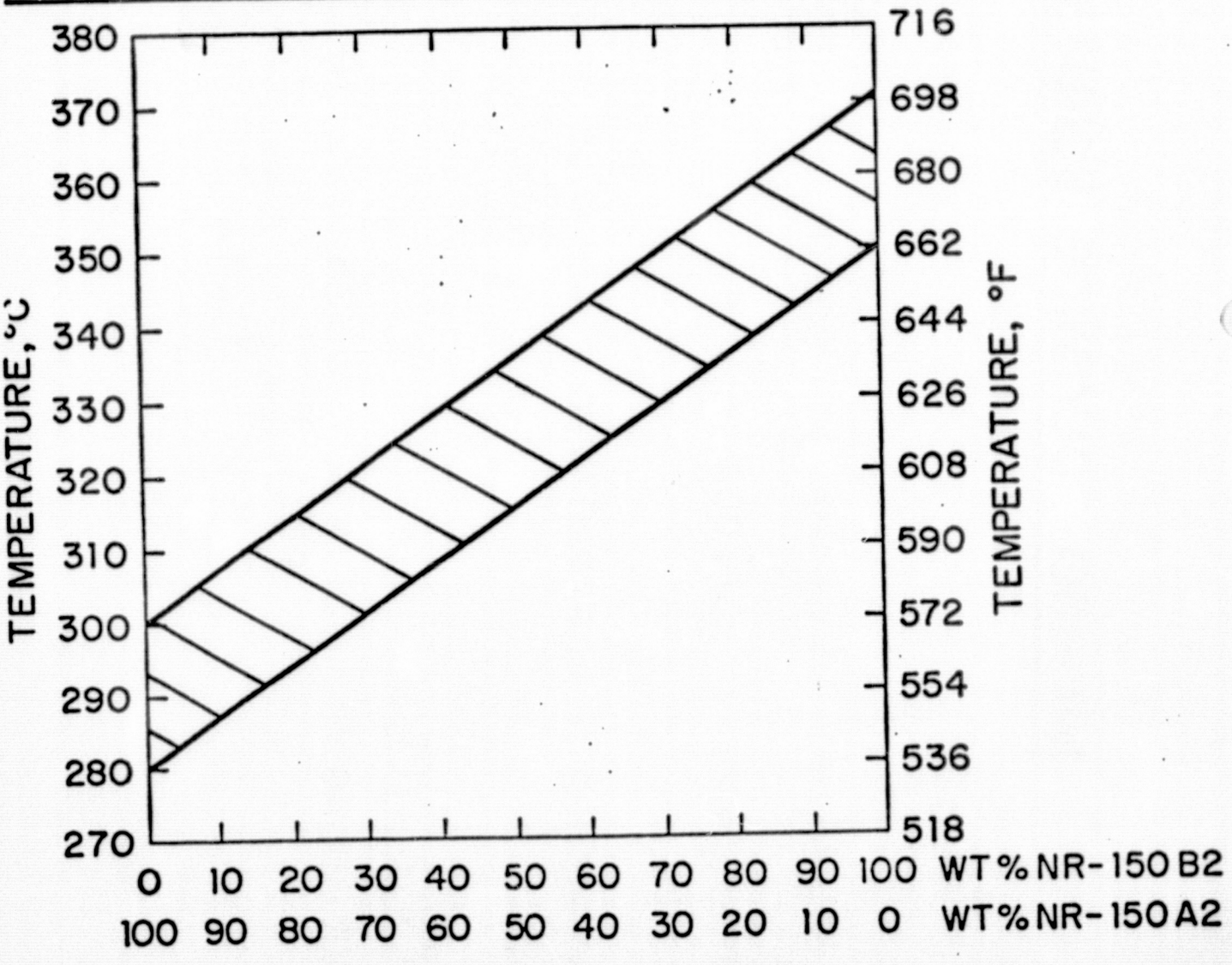
662-700°F

NR-150 POLYIMIDE SOLUTIONS

BINDER TYPE	MONOMERS	% SOLIDS	VISCOSITY, POISES	T_g
NR-150A2	6F/ODA	45	50	536-572°F 280-300°C
NR-150B2	6F/PPD/MPD	45	125	662-700°F 350-371°C
ADHESIVE TYPE				
NR-150AG	6F/ODA PAA	35	1000-3000	536-572°F 280-300°C

FIGURE 2

EFFECT OF NR-150 BINDER COMPOSITION ON GLASS TRANSITION TEMPERATURE



KEY FEATURES OF NR-150 POLYIMIDES

- AMORPHOUS
- LINEAR
- HIGH MOLECULAR WEIGHT

] TOUGHNESS

- THERMOPLASTIC ABOVE T_g] LOW VOIDS
- T_g CONTROL] PROCESS OPTIMIZATION
  HIGH TEMPERATURE PROPERTY RETENTION
- "ALL AROMATIC"] THERMAL-OXIDATIVE STABILITY

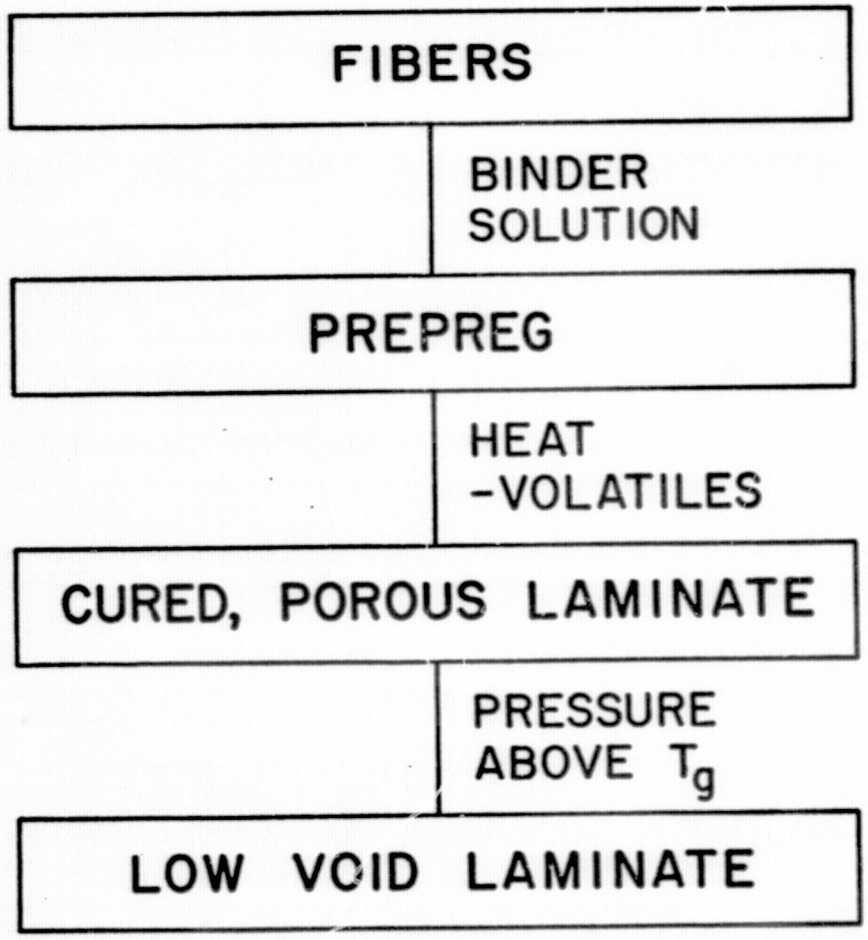
NEAT RESIN PROPERTIES

	NR-150A2	NR-150B2
T_g	280 - 300°C 536 - 572°F	350 - 371°C 662 - 700°F
TENSILE STRENGTH, psi		
23°C (73°F)	16,000	16,000
260°C (500°F)	4,300	
316°C (600°F)		4,500
ELONGATION, %		
23°C (73°F)	8	6
260°C (500°F)	69	
316°C (600°F)		65

NR-150 PROCESSING VERSATILITY

- VACUUM BAG / AUTOCLAVE MOLDING
  - HEATED AUTOCLAVE
  - HEATED TOOLING
- COMPRESSION MOLDING
- THERMOFORMING
- ULTRASONIC MOLDING
- THICK SECTIONS (NO PRECIPITATION)
- NO MATRIX CRACKING (TOUGHNESS)
- VERY FORGIVING

6F POLYIMIDE LAMINATE PREPARATION



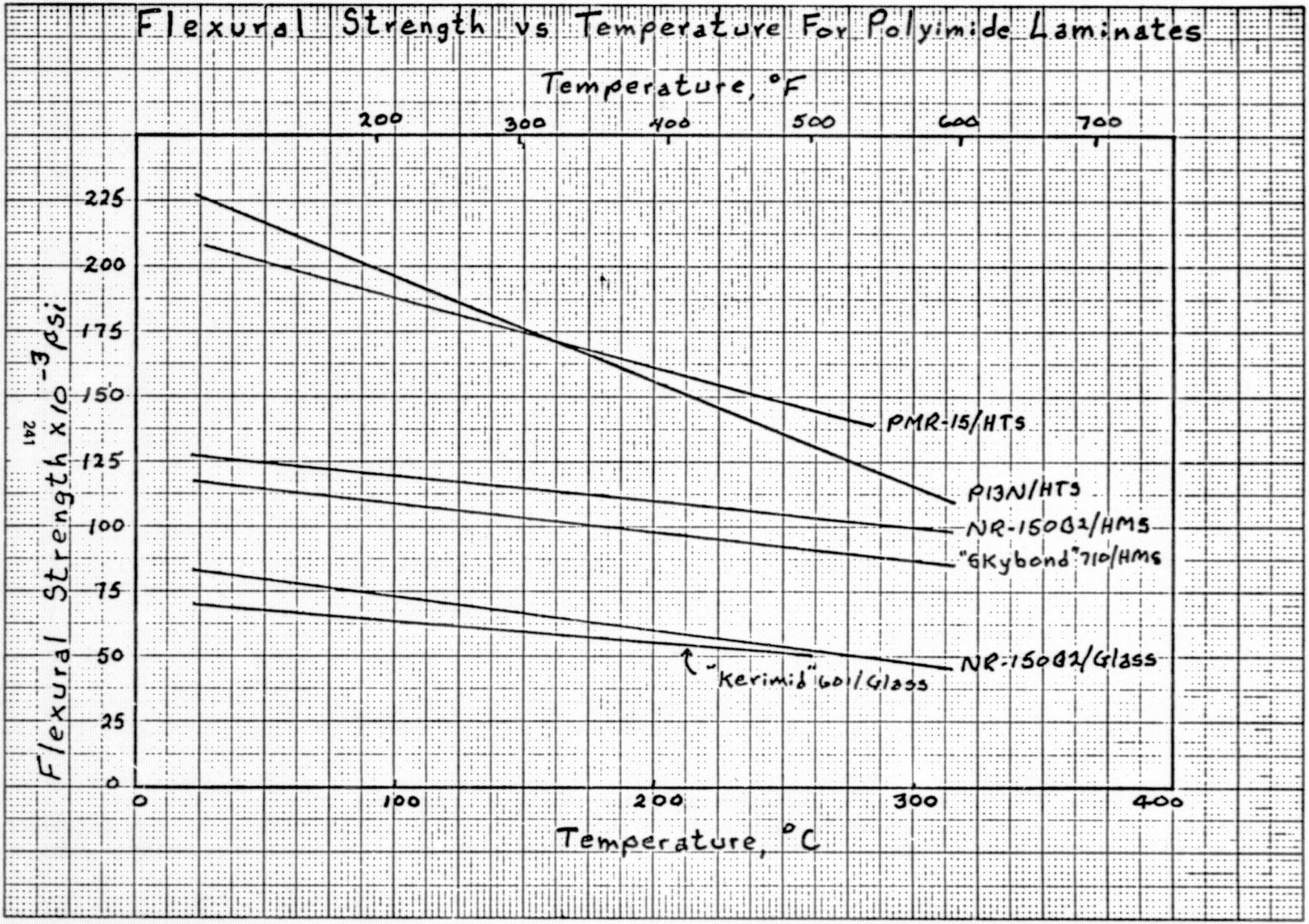
GRAPHITE FIBER / NR-150 COMPOSITES

- LOW VOID CAPABILITY
- ADHERES WELL TO ALL GRAPHITE FIBERS
- AT LEAST 9000 psi SHORT BEAM SHEAR STRENGTH RETENTION AT 600°F
- THERMAL-OXIDATIVE STABILITY
- THICK LAMINATE CAPABILITY
- CRACK-FREE X-PLY LAMINATES

HMS GRAPHITE / NR-150B2
UNIDIRECTIONAL LAMINATES

MECHANICAL PROPERTIES	73°F (23°C)	600°F (316°C)	650°F (343°C)
FLEXURAL STRENGTH M PSI	126	99	72
FLEXURAL MODULUS MM PSI	21	20	17
SHORT BEAM SHEAR STRENGTH M PSI	7.4	4.6	4.6

GRAPH PAPER GRAPHIC CONTROLS CORPORATION Buffalo, New York
Printed in U.S.A.
SQUARE 10 X 10 TO THE HALF INCH



NR-150 AG ADHESIVE

SUBSTRATES STUDIED:

TITANIUM
ALUMINUM
STAINLESS STEEL
MECHANICAL CARBON
VESPEL® SP PARTS

PROCESSING FEATURES:

- PRECURE IN THE OPEN
- FUSE UNDER PRESSURE ABOVE T_g

TYPICAL RESULTS FOR 6-4 TITANIUM LAP JOINTS:

LAP SHEAR STRENGTH: −320°F = 6000 psi
73°F = 5000 psi
500°F = 3000 psi

ENVIRONMENTAL EFFECTS

MOISTURE – UNUSUALLY GOOD HYDROLYTIC STABILITY

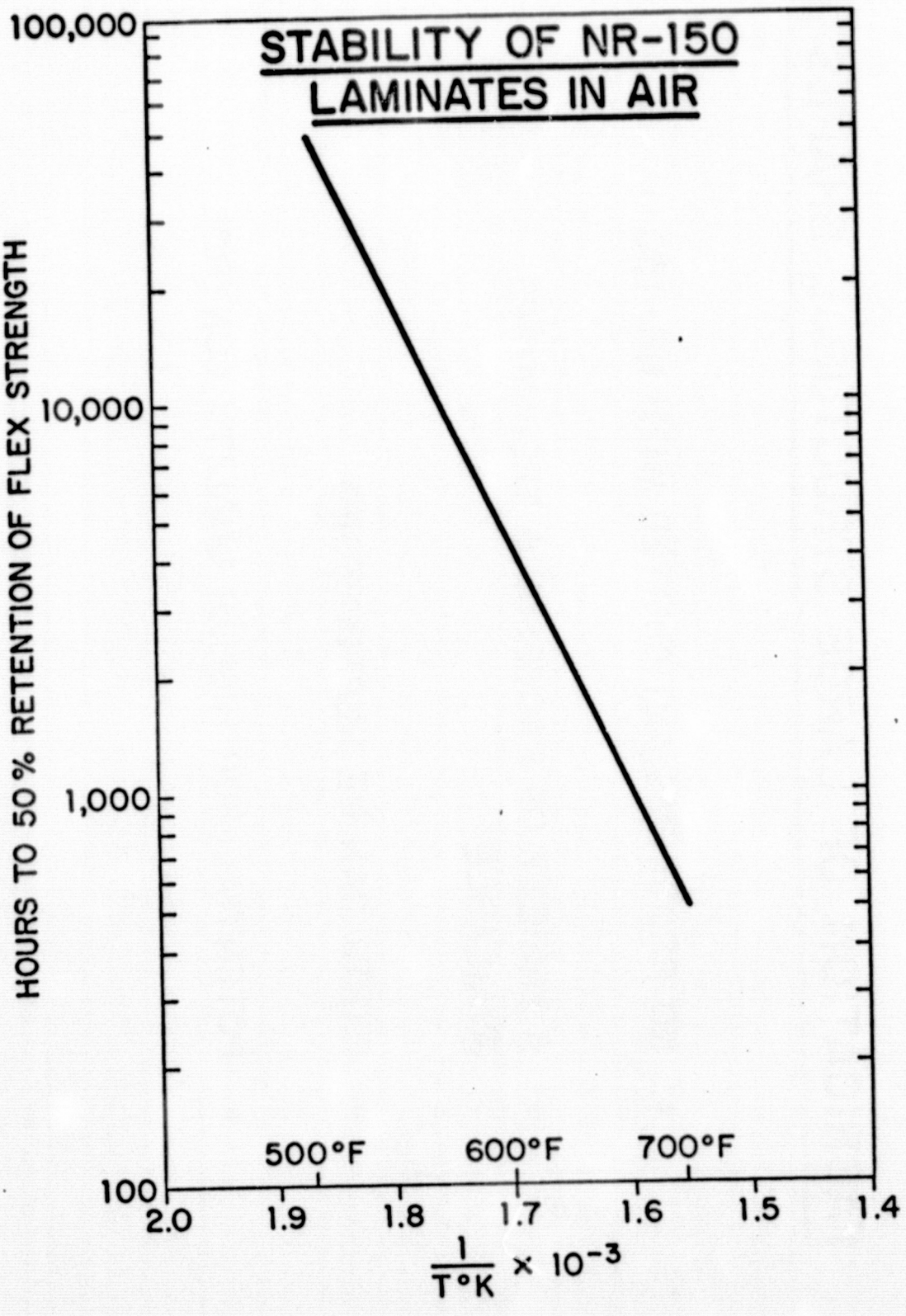
FUELS – VERY RESISTANT TO HYDROCARBONS

VACUUM – VERY LOW VACUUM OUTGASSING

RADIATION – VERY RESISTANT TO HIGH ENERGY RADIATION

AIR AGEING OF QUARTZ FABRIC/NR-150A LAMINATES AT 500°F (260°C)

	TESTED AT 482°F (250°C)		
	INITIAL	10,000 HRS.	20,000 HRS.
FLEX STRENGTH, PSI	53,100	51,900	
FLEX MODULUS, PSI	3.2×10^6	2.9×10^6	
SHORT BEAM SHEAR STRENGTH, PSI	4,200	5,000	4,900
T_G, °F	518	541	565
°C	270	283	295
% WEIGHT LOSS	---	2.3	3.0


STABILITY OF NR-150
LAMINATES IN AIR
HOURS TO 50 % RETENTION OF FLEX STRENGTH
100,000
10,000
1,000
100
500°F
600°F
700°F
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1/T°K x 10⁻³

FABRICATION OF LARGE STRUCTURAL SHAPES

- NO PROBLEMS ANTICIPATED WITH NR-150
- A VARIETY OF PROCESSING TECHNIQUES AVAILABLE
- PARTS CAN BE REPROCESSED
- POTENTIAL FOR HIGHER QUALITY CONTROL

NR-150 AVAILABILITY AND QUALITY CONTROL

- ALL MONOMERS MADE WITHIN DUPONT
- MONOMER PURITY RIGIDLY CONTROLLED
- ALL BINDER AND ADHESIVE SOLUTIONS MADE WITHIN DUPONT
- NR-150 SOLUTIONS UNDER TIGHT QUALITY CONTROL
- BOTH THE MONOMERS AND SOLUTIONS MADE IN EXISTING FACILITIES
- CAPACITY TO BE EXPANDED AS REQUIRED

HEALTH HAZARDS – GOVERNMENT REGULATIONS

- NO EPA OR OSHA REGULATIONS – NONE ANTICIPATED
- TESTS TO DATE INDICATE MONOMERS ARE NOT CARCINOGENIC
- EXPOSURE TO NMP SHOULD BE AVOIDED

NR-150 SOLUTIONS – TYPES OF APPLICATIONS

LAMINATING RESINS

ADHESIVES

COATINGS

CHOPPED FIBER MOLDING

RESULT – STRONGER BUSINESS POSITION THROUGH A BROAD APPLICATION BASE

NR-150 ECONOMICS

CURRENT SELLING PRICES:

BINDER SOLUTIONS – $65 per pound*

ADHESIVE SOLUTION – $75 per pound*

*CURED RESIN SOLIDS. INCLUDES $2 per pound ROYALTY

LONG TERM SELLING PRICE:

- WILL BE VOLUME DEPENDENT
- WILL COST MORE THAN CONVENTIONAL PI BINDERS

SUMMARY

NR-150 POLYIMIDE SOLUTIONS OFFER:

- DUPONT QUALITY CONTROL OF MONOMERS AND SOLUTIONS
- LOW TOXICITY - NO GOVERNMENT REGULATIONS
- PROCESSING VERSATILITY
- LOW VOIDS
- HIGH MECHANICAL PROPERTY LEVELS
- ULTIMATE IN THERMAL-OXIDATIVE STABILITY
- TOUGHNESS
- BROAD APPLICATION BASE
- POTENTIAL FOR HIGH QUALITY YIELD IN FABRICATED PARTS

GENERAL DYNAMICS PRESENTATION

GENERAL DYNAMICS PRESENTATION

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HIGH-TEMPERATURE RESIN-MATRIX COMPOSITES

17 March 1975

Prepared by
GENERAL DYNAMICS CONVAIR DIVISION
P.O. Box 80847
San Diego, California 92138

CONVENTIONAL POLYIMIDES

RESIN	CURE PARAMETERS	POST CURE	EVOLUTION OF VOLATILES IN CURE	HYDROLYTIC STABILITY	THERMAL/ OXIDATIVE STABILITY	VOIDS	THICK LAMINATE CAPABILITY	HANDLING (DRAPE TACK)	DEGREE OF TECH. DEVELOP.	COST
MONSANTO 710 POLYIMIDE (PI)	350F, VAC. BAG MIN.	TO 700F NO P	HIGH	EXCELLENT	TO 600F	< 5%	YES, VAC. BAG ONLY	EXCELLENT	HIGH	LOW
MONSANTO 700 & 703 (PI)	350F, VAC. BAG ONLY	TO 700F NO P	HIGH	EXCELLENT	TO 600F	10%	NO, HIGH VOIDS	EXCELLENT	HIGH	LOW
DuPONT 4707 (PI)	350F, VAC. BAG ONLY	TO 700F, NO P	HIGH	EXCELLENT	TO 600F	10%	NO, HIGH VOIDS	EXCELLENT	HIGH	LOW

OTHER RESIN SYSTEMS

POLYQUINOXYALINE (PQ)	750F, 50 PSI MIN.	TO 850F, 100 PSI	LOW	EXCELLENT	THERMAL – 600F OXIDATIVE – 500F	< 5%	YES, UNDER HIGH PRES.	LOW TO POOR	MODERATE	VERY HIGH
POLYPHENYLQUIN-OXALINE (PPQ)	750F TO 800F, 50 PSI MIN.	TO 850F, 100 PSI	LOW	EXCELLENT	TO 600F	< 5%	YES, UNDER HIGH PRES.	LOW TO POOR	MODERATE	VERY HIGH
POLYBENZIMIDAZOLE (PBI)	700F 200 PSI MIN	TO 800F	VERY HIGH	GOOD	THERMAL – 600F OXIDATIVE – 450F	< 10%	NO, HIGH VOIDS	POOR	HIGH	HIGH
X350 (POLYTRIAZINE)	350 TO 375F, 50 TO 100 PSI	TO 700F	VARIABLE	VERY POOR	TO 500F	< 10%	NO, HIGH VOIDS	GOOD	LOW	HIGH

254

26063CVD7351

SECOND-GENERATION POLYIMIDES
Thermoplastic and Addition Types

GENERAL DYNAMICS
Convair Division

RESIN	CURE PARAMETERS	POST CURE	EVOLUTION OF VOLATILES IN CURE	HYDROLYTIC STABILITY	THERMAL/ OXIDATIVE STABILITY	VOIDS	THICK LAMINATE CAPABILITY	HANDLING (DRAPE & TACK)	DEGREE OF TECH. DEVELOP.	COST
DuPONT NR150 SERIES (PI)	800F, 200 PSI	NONE	LOW	EXCELLENT	TO 600F	< 5%	YES, HIGH P	POOR, BUT IMPROVES WHEN HEATED	LOW	VERY HIGH
UPJOHN 2080 (PI)	700F, 200 PSI	NONE	LOW	GOOD	TO 550F	< 5%	YES, HIGH P	POOR BUT IMPROVES WHEN HEATED	LOW	MODERATE
P13N (PI)	600F, 100 PSI, 10F/MIN. HEAT-UP RATE REQ.	NONE	LOW	GOOD	TO 550F	< 5%	YES, 50-100 PSI REQ.	POOR, A HIGH VOL. TACKY VERSION AVAIL.	HIGH	MODERATE
P105A (PI)	575F, 50 PSI MIN.	TO 600F, NO P	LOW	GOOD	TO 550F	< 5%	YES, 50-100 PSI REQ.	MODERATE	LOW/MED.	MODERATE
KERIMID 601 (PI)	360F, VAC. BAG MIN.	480 TO 500F, NO P	LOW	GOOD	TO 475F	< 5%	YES, 50-100 PSI REQ.	LOW TACK & DRAPE	LOW/MED.	MODERATE
DuPONT 3003 (PI)	360F, VAC. BAG MIN.	475 TO 500F, NO P	LOW	GOOD	TO 475F	< 5%	YES, 50-100 PSI REQ.	LOW TO MODERATE	LOW	MODERATE
BRUNSWICK BPI-373 (PI)	TO 600F, 100 TO 200 PSI	NONE	LOW	GOOD	TO 550F	< 5%	YES, HIGH P	VERY POOR	MODERATE	HIGH

HIGH-TEMPERATURE SYSTEMS EVALUATED BY CONVAIR

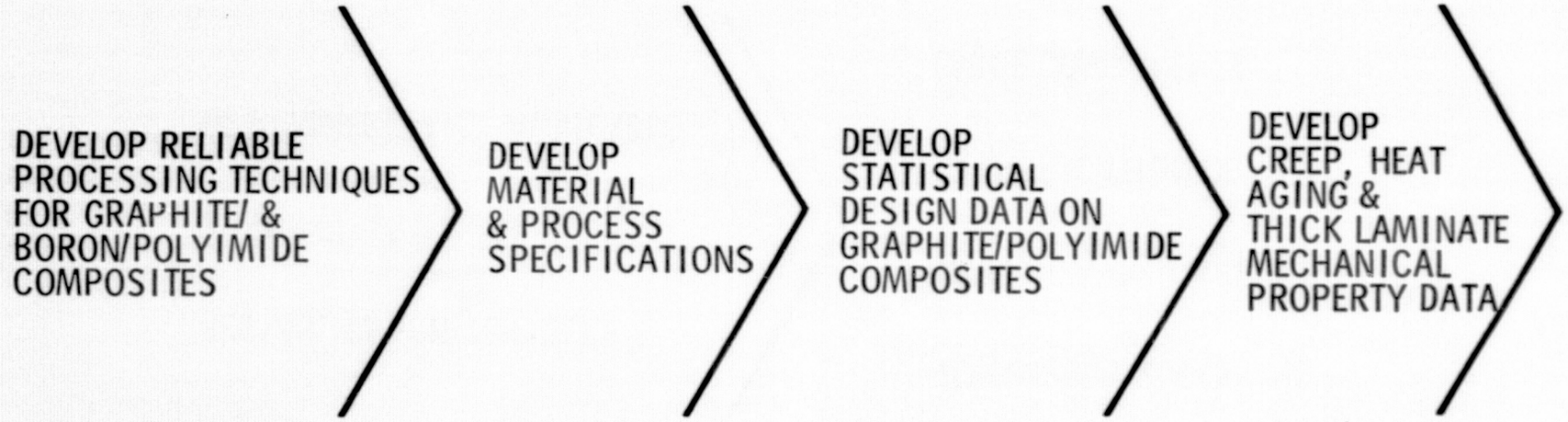
GLASS/QUARTZ	GRAPHITE	BORON
700	HT-S/710	B/703M
703	HM-S/710	B/703
RS 6228	GY-70/710	B/710
RS 6234	TYPE AS/710	B/P105A
P13N	MOD I/710	
PBI	MOD II/710*	
	4R/710*	
	4R/P105A	
	HT-S/P105A	
	HM-S/P105A	
	4R/3003*	
	4R/2001	
	HT-S/703	
	HT-S/4707	
	GY-70/4707	
	HT-S/PQ	
	HT-S/PPQ	

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26063CVD7358

PROGRAM OBJECTIVES

GENERAL DYNAMICS
Convair Division



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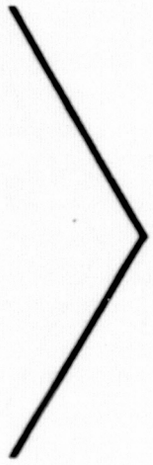
72-2896

PROGRAM GUIDELINES

RESINS, GRAPHITE FIBERS &

BORON FIBERS MUST

BE COMMERCIALLY AVAILABLE



DEVELOPED PROCESSING

MUST BE APPLICABLE

TO FABRICATION OF

LARGE COMPONENTS

AVAILABLE GRAPHITE & BORON FIBERS

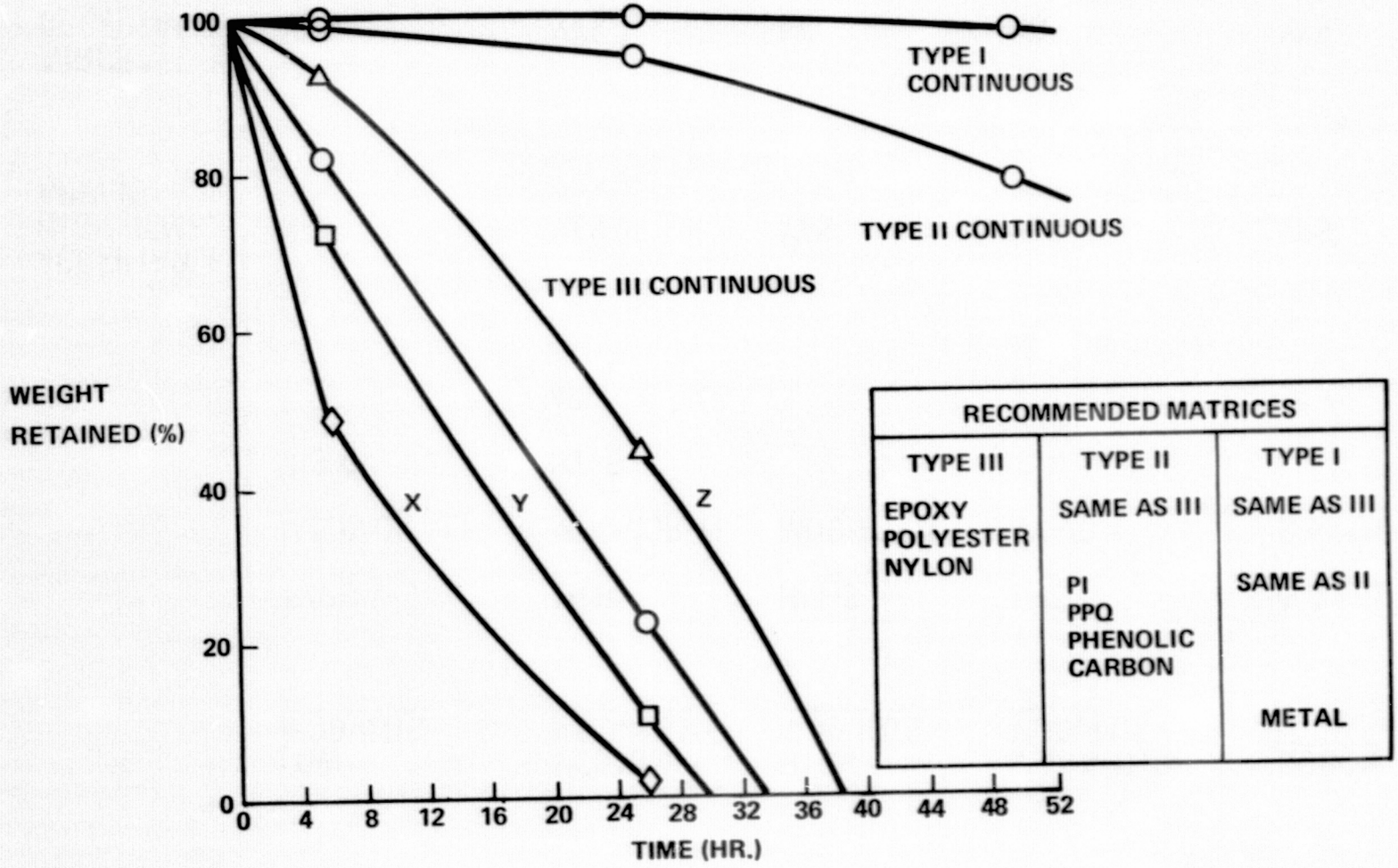
GENERAL DYNAMICS
Convair Division

	LOW MODULUS	MEDIUM MODULUS	HIGH MODULUS	ULTRA-HIGH MODULUS	BORON
	TYPE A-S	T-400	HM-S	T-75	4.0 MIL
	MODMOR III	MODMOR II	MODMOR I	GY-70	5.6 MIL
	T-300	HT-S			
		4R			
ACCEPTABLE HIGH-TEMP. APPLIC.	NO	YES	YES	YES	YES
AIRCRAFT ACCEPTABLE	YES	YES	NO	NO	YES

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26063CVD7359

OXIDATION STUDY OF MODMOR FIBER IN STILL AIR AT 400C



RECOMMENDED MATRICES		
TYPE III	TYPE II	TYPE I
EPOXY POLYESTER NYLON	SAME AS III	SAME AS III
	PI PPQ PHENOLIC CARBON	SAME AS II
		METAL

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26063CVD7360

GENERAL DYNAMICS
Convair Division

GRAPHITE/POLYIMIDE (710)
Design Data

	TENSILE	COMP.	FLEX.	SHEAR	CREEP	FATIGUE	BEARING	AGING
• HT-S (SHORT)*	X	X	X	X	X			
• HT-S (CONTINUOUS) (HERCULES)	X	X	X	X				
• HT-S (CONTINUOUS) (COURTAULDS)	X		X	X				
• HT-S* (CONTINUOUS)	X	X	X	X	X	X	X	X
• HM-S* (CONTINUOUS)	X	X	X	X		X		X
• GY-70	X	X	X	X				

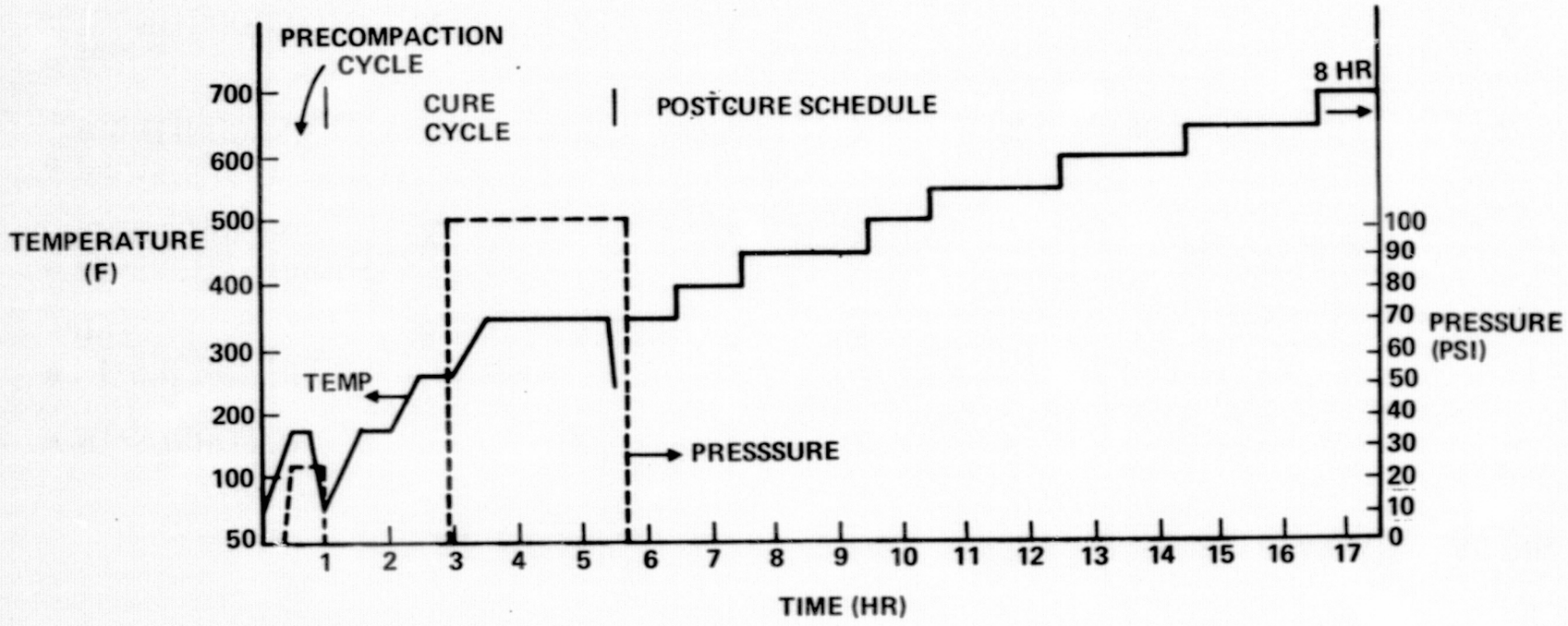
261

*MOISTURE RESISTANCE, HUMIDITY, CORROSION, FUEL & STACK GAS RESISTANCE EVALUATED OR CURRENTLY BEING EVALUATED

14035CVD7356A

SKYBOND 710 CURE SCHEDULE

GENERAL DYNAMICS
Convair Division



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07025CVF7105

PRELIMINARY DESIGN PROPERTIES
HT-S/710
GRAPHITE/POLYIMIDE COMPOSITE

GENERAL DYNAMICS
Convair Division

LAMINATE DIRECTION	TEST DIRECTION	TEST TEMPERATURE (°F)	ULTIMATE STRESS (KSI)	MODULUS
0°	0° TENSION	-320	137.7	19.9
		75	165.7	23.0
		600	162.0	20.8
	45° TENSION	-320	6.1	
		75	4.6	
		600	3.4	
	90° TENSION	-320	2.6	
		75	2.8	
		600	1.5	

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72-2134

PRELIMINARY DESIGN PROPERTIES (Cont.)

GENERAL DYNAMICS
Convair Division

HT-S/710
GRAPHITE/POLYIMIDE COMPOSITE

LAMINATE DIRECTION	TEST DIRECTION	TEST TEMPERATURE (°F)	ULTIMATE STRESS (KSI)	MODULUS
$[0, \pm 45^\circ]_{2S}$	0° TENSION	-320	65.8	
		75	68.7	
		600	69.3	
	0° COMPRESSION	-320	60.3	
		75	68.7	
		600	42.6	
$[0, \pm 45^\circ, 90]_{2S}$	0° TENSION	-320	43.6	
		75	43.1	
		600	46.7	
	0° COMPRESSION	-320	54.5	
		75	47.8	
		600	37.0	

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72-2137

GENERAL DYNAMICS
Convair Division

TENSILE STRENGTH OF HT-S/710 GRAPHITE/POLYIMIDE AS FUNCTION OF TEMPERATURE

TEST TEMPERATURE (°F)	LONGITUDINAL TENSILE STRENGTH (KSI)	MODULUS (10^6 PSI)
75	173.2	21.5
350	161.7	–
500	160.9	–
600	162.0	–
650	151.1	21.5
700	145.4	21.1
800	99.8*	–

*FAILED IN GRIP AREA

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72-2122

GENERAL DYNAMICS
Convair Division

HEAT-AGING OF HT-S/710 GRAPHITE/POLYIMIDE COMPOSITE AT 600°F

HOURS AT 600°F	TENSILE STRENGTH (KSI)		FLEXURAL STRENGTH (KSI)	
	75°F	600°F	75°F	600°F
0	161.1	162.0	212.3	135.0
100	165.2	164.9	217.5	148.9
200	149.4	153.4	204.4	151.1
400	168.4	150.1	213.5	121.4

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72-2133

HIGH MODULUS GRAPHITE/POLYIMIDE COMPOSITE SYSTEMS 710 RESIN

GENERAL DYNAMICS
Convair Division

TYPE OF FIBER	FLEXURAL STRENGTH (KSI)			INTERLAMINAR SHEAR (KSI)		
	-320°F	75°F	600°F	-320°F	75°F	600°F
HM-S	142.4	133.6	116.6	5.90	6.18	5.16
MOD I	106.3	112.9	114.0	6.92	6.45	5.52
6T	–	91.9	77.2	–	4.19	4.15
GY-70	79.5	98.3	94.1	4.83	5.20	4.22

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10/16/72-4715

MODMOR I/710 GRAPHITE/POLYIMIDE COMPOSITES

Test Results

TEST TEMP (F)	FLEXURAL STRENGTH (KSI)	FLEXURAL MODULUS (10^6 PSI)	SHORT BEAM SHEAR STRENGTH (KSI)
75	118	30	5.0
	124	28	4.9
	149	25	4.8
	130	27	4.9
350	147	25	5.3
	145	25	4.7
	143	26	4.8
	145	25	5.0
600	129	22	3.8
	118	23	4.5
	134	22	4.5
	127	23	4.3

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SPECIFIC GRAVITY 1.55

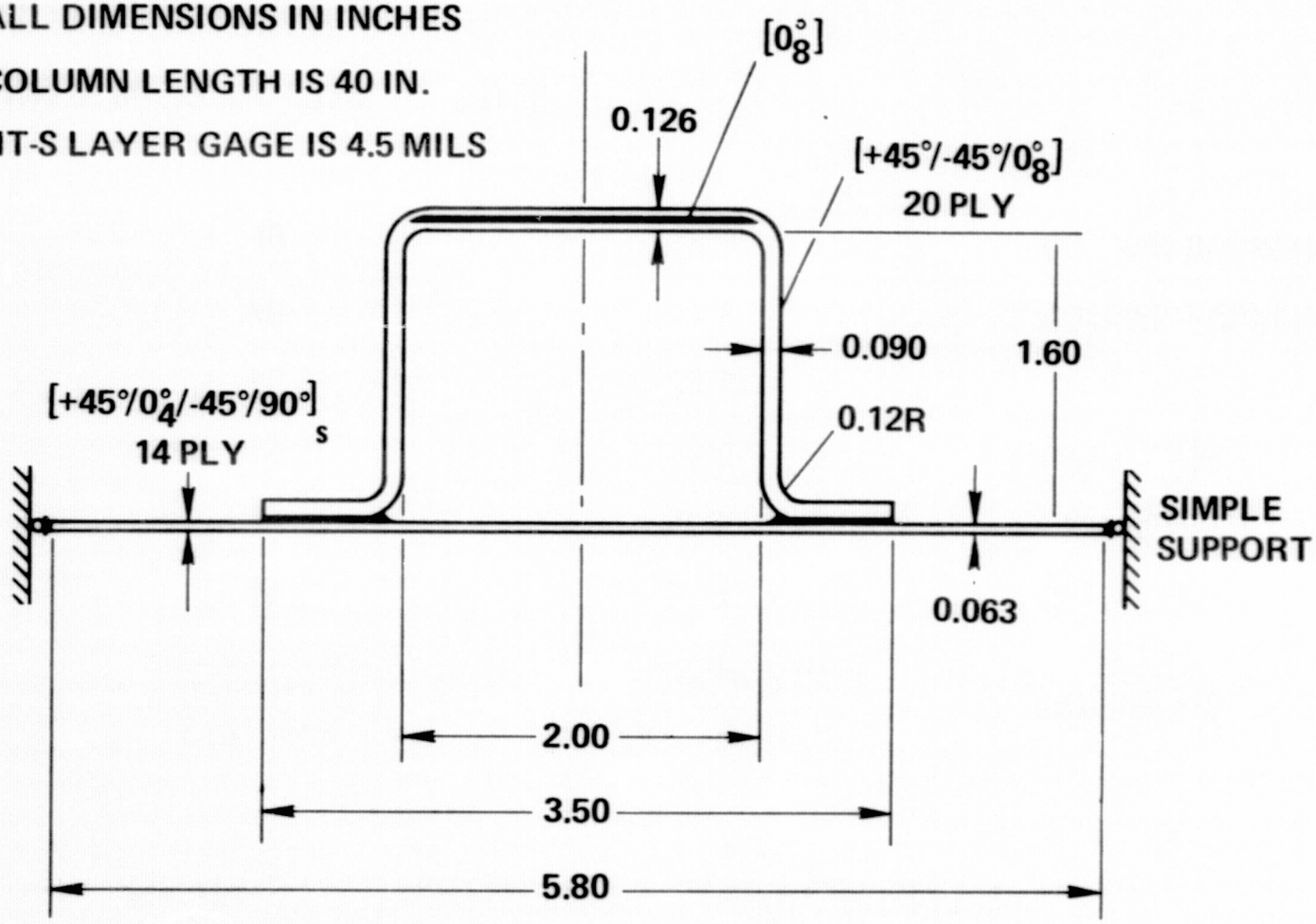
RESIN CONTENT 25.4

07025CVF7115

HT-S GRAPHITE/POLYIMIDE

NOTE

1. ALL DIMENSIONS IN INCHES
2. COLUMN LENGTH IS 40 IN.
3. HT-S LAYER GAGE IS 4.5 MILS



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71-1233

GENERAL DYNAMICS
Convair Division

GRAPHITE/POLYIMIDE (HT-S/710) SKIN-STRINGER TEST COMPONENTS

SPECIMEN NO.	STRINGER LENGTH (IN.)	FAILURE LOAD (10^3 LB)	FAILURE MODE
1	15	55.7	CRIPPLING
2	15	57.5	CRIPPLING
3	15	59.0	CRIPPLING
4	40	23.8*	—
5	40	44.9	COLUMN BUCKLING
6	40	49.3	COLUMN BUCKLING

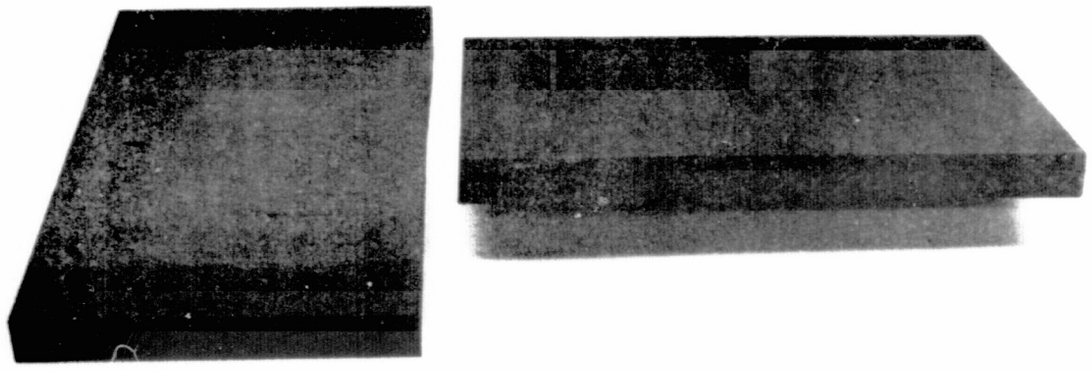
DESIGN ULTIMATE BUCKLING LOAD: 42,800 LB

*FAILURE DUE TO PLY ORIENTATION

270

14035CVF7234

1" THICK HT-S/710 PANELS

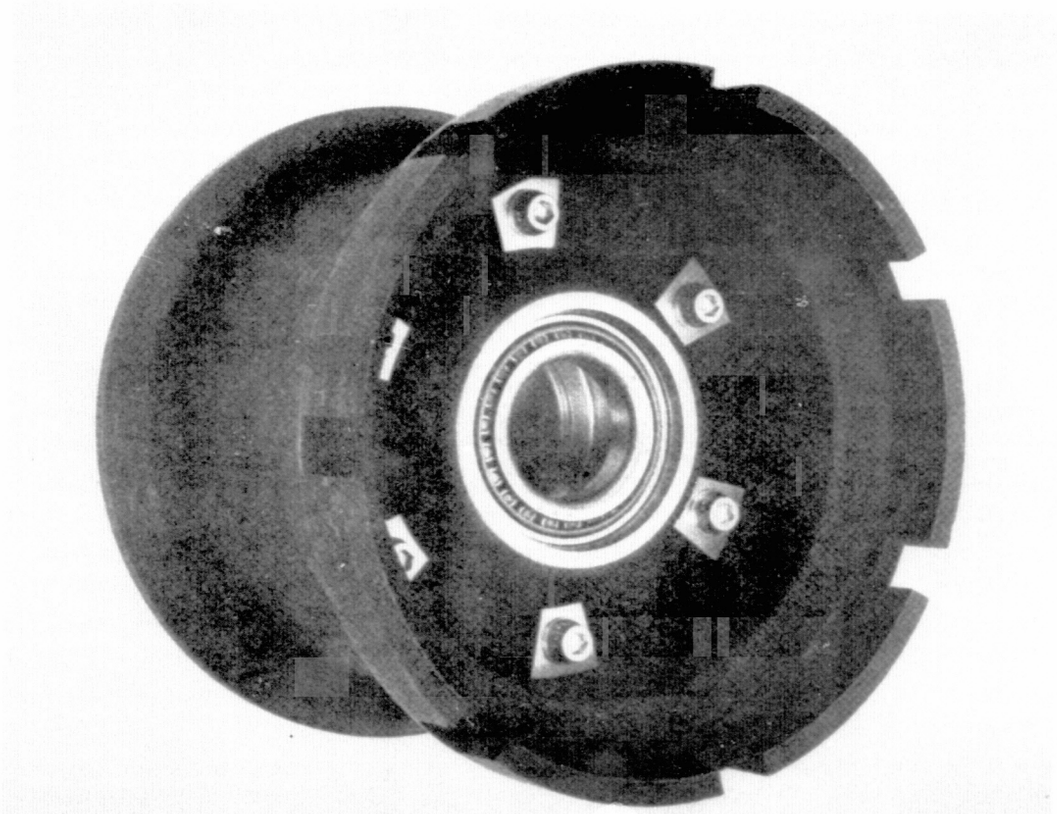


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14035CVF7109A

GRAPHITE/POLYIMIDE WHEEL FOR A-37

GENERAL DYNAMICS
Convair Division



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07025CVF7110

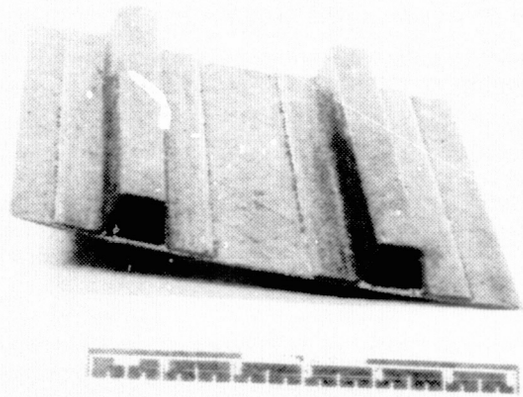
CONVAIR-DEVELOPED
GRAPHITE-ASBESTOS/POLYIMIDE SUBELEMENT COMPOSITES

GENERAL DYNAMICS
Convair Division

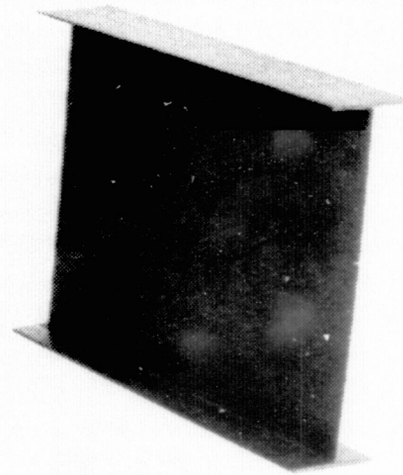
273



SANDWICH BEAM COMPOSITE



STIFFENED PANEL COMPOSITE



I-BEAM COMPOSITE

07025CVF7123

EVALUATION OF P105A
GRAPHITE/POLYIMIDE COMPOSITES

GENERAL DYNAMICS
Convair Division

GRAPHITE FIBER	TEST TEMP (F)	FLEX STR (KSI)	SHEAR STR (KSI)	TENSILE STR (KSI)	FIBER VOL (%)	RESIN CONTENT (%)	SPECIFIC GRAVITY
HM-S	75	90	6.9	—			
	600	92	5.1	115			
HT-S	75	205	9.0	157			
	600	150	5.5	174			
4R	75	244	8.1	199	67	28	1.5
	600	175	5.5	223			

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07025CVF7122

GENERAL DYNAMICS
Convair Division

HT-S/601 GRAPHITE/POLYIMIDE PROPERTIES

TEST TEMP (F)	CONTROL LONG FLEX (KSI)	24 HR H_2O BOIL 0° FLEX	100 HR AGING AT 450F 0° FLEX	500 HR AGING AT 450F 0° FLEX
75	211	183	221	162
	203	178	204	226
	206	161	225	124
	207	174	216	171
450	57	49	85	49
	70	34	81	69
	48	37	63	70
	58	40	76	62
	SBS (KSI)	SBS (KSI)	SBS (KSI)	SBS (KSI)
75	12	8	11	12
	12	9	13	9
	12	9	11	13
	12	9	12	11
450	3.0	1.6	2.1	4.9
	2.6	1.7	2.0	3.9
	2.4	1.8	2.9	3.6
	2.7	1.7	2.3	4.2

LAMINATE NO. 7	
%FIBER VOLUME	60.3
% RESIN CONTENT	32.7
SPECIFIC GRAVITY	1.55
% VOID	1.4

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07025CVF7120

HT-S/3003 GRAPHITE/POLYIMIDE PROPERTIES

TEST TEMP (F)	CONTROL LONG FLEX (KSI)	24 HR H_2O BOIL 0° FLEX	100 HR AGING AT 450F 0° FLEX	500 HR AGING AT 450F 0° FLEX
75	234	182	228	224
	203	183	210	224
	225	177	191	196
	221	181	209	215
450	100	29	127	177
	106	28	141	158
	112	27	145	165
	106	28	138	167
	SBS (KSI)	SBS (KSI)	SBS (KSI)	SBS (KSI)
75	12	10	12	11
	14	11	13	11
	13	9	13	11
	13	10	13	11
450	3.6	2.0	7.5	7.8
	4.1	2.0	7.5	7.3
	4.1	1.7	7.8	8.0
	4.0	1.9	7.6	7.7

LAMINATE NO. 9		
% FIBER VOLUME		62.8
% RESIN CONTENT		32.0
SPECIFIC GRAVITY		1.52
% VOID	6.5	6.5

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07025CVF7119

MODMOR II/HX-580

GRAPHITE/POLYIMIDE PROPERTIES

TEST TEMP (F)	CONTROL LONG FLEX (KSI)	24 HR H_2O BOIL (0F)	100 HR AGING AT 450F (0F)	500 HR AGING AT 450F (0F)
75	203	173	219	213
	196	182	192	190
	187	197	217	223
	195	184	210	209
450	99	82	159	152
	98	75	158	152
	96	80	184	153
	97	79	167	152
	SBS (KSI)	SBS (KSI)	SBS (KSI)	SBS (KSI)
75	9.2	8.9	8.4	6.5
	7.8	7.9	9.7	6.0
	8.9	8.1	6.3	6.5
	8.6	8.3	8.2	6.4
450	4.2	3.4	7.8	7.5
	4.1	2.8	5.9	6.7
	4.2	2.9	6.4	7.2
	4.2	3.0	6.7	7.2

LAMINATE NO. 15	
% FIBER VOLUME	57.9
% RESIN CONTENT	34.8
SPECIFIC GRAVITY	1.57
% VOID	0.0

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07025CVF7116

PROCESS EVALUATION STUDY (CURE CYCLE NO. 1)
MODMOR II/HX-580 Graphite/Polyimide

TEST TEMP (F)	TYPE OF TEST	LAM 15 FLEX STR (KSI)	LAM 15 SBS STR (KSI)	LAM 19 FLEX STR (KSI)	LAM 19 SBS STR (KSI)	LAM 20 FLEX STR (KSI)	LAM 20 SBS STR (KSI)
75	INITIAL	203	9.2	220	8.9	245	7.6
		196	7.8	240	9.4	243	8.4
		187	8.9	237	9.0	208	8.6
		195	8.7	232	9.1	232	8.2
450	INITIAL	99	4.2	204	5.8	173	7.3
		98	4.1	178	6.4	162	89
		96	4.2	170	6.8	159	7.8
		97	4.2	184	6.3	165	8.0
75	24 HR H_2O BOIL	173	8.9	223	6.5	221	5.9
		182	7.9	219	8.0	223	7.2
		197	8.1	195	8.4	191	7.0
		184	8.3	212	7.7	211	6.8
450	24 HR H_2O BOIL	82	3.4	133	4.1	121	3.7
		75	2.8	133	3.8	125	5.1
		80	2.9	137	3.7	147	5.7
		79	3.1	134	3.9	131	4.9
FIBER VOLUME		57.9		59.7		61.6	
RESIN CONTENT		34.8		33.0		31.2	
SPECIFIC GRAVITY		1.57		1.54		1.54	
VOID CONTENT		0.0		1.3		2.0	

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07025CVF7114

GENERAL DYNAMICS
Convair Division

PROCESS EVALUATION STUDY (CURE CYCLE NO. 2)

MODMOR II/HX-580 Graphite/Polyimide

TEST TEMP (F)	TYPE OF TEST	LAM 21 FLEX STR (KSI)	LAM 21 SBS STR (KSI)	LAM 22 FLEX STR (KSI)	LAM 22 SBS STR (KSI)	LAM 23 FLEX STR (KSI)	LAM 23 SBS STR (KSI)
75	INITIAL	201	9.3	240	8.9	270	7.5
		208	8.8	212	8.7	245	7.7
		205	10.5	220	8.6	250	8.4
		205	9.6	224	8.8	255	7.9
450	INITIAL	154	8.0	203	8.3	139	7.5
		164	6.8	167	7.9	176	7.8
		131	8.3	150	8.1	162	8.0
		158	7.8	173	8.2	159	7.8
75	24 HR H_2O BOIL	211	7.5	234	7.9	244	7.9
		197	7.5	188	7.9	189	7.0
		228	8.3	231	7.2	198	7.9
		212	7.8	218	7.7	204	7.6
450	24 HR H_2O BOIL	118	4.1	116	4.5	120	4.4
		112	3.9	99	4.4	141	4.5
		111	4.3	110	3.9	136	5.9
		114	4.1	108	4.3	132	4.9
FIBER VOLUME		57.0		60.9		63.5	
RESIN CONTENT		35.5		32.0		29.7	
SPECIFIC GRAVITY		1.54		1.54		1.53	
VOID CONTENT		0.6		1.7		3.0	

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07025CVF7113

POTENTIAL COMPOSITE APPLICATIONS
Space Shuttle Orbiter

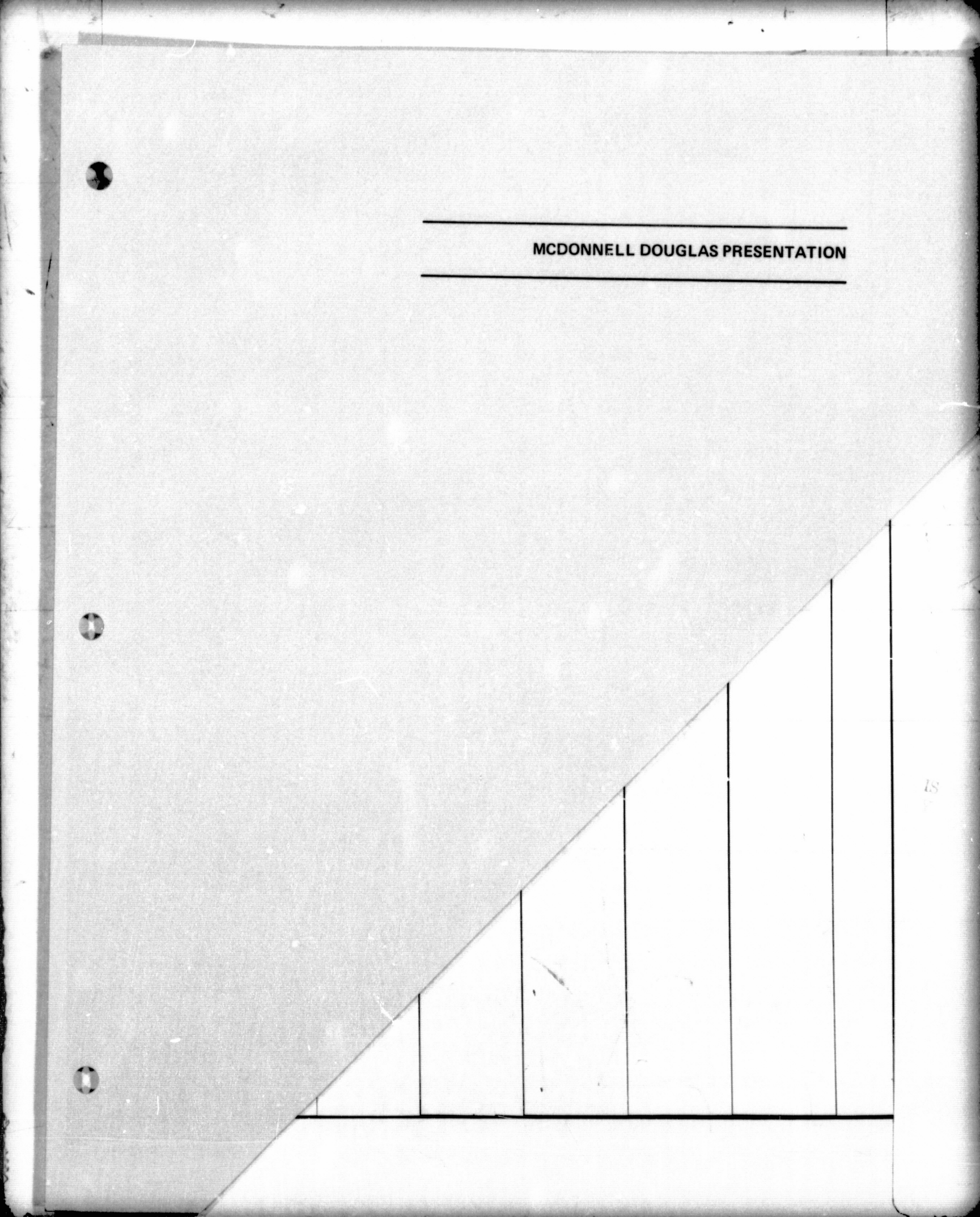
GENERAL DYNAMICS
Convair Division

	WEIGHT SAVING (LB)	TYPE OF DESIGN
GRAPHITE/POLYIMIDE		
BODY FLAP	200	SANDWICH
PAYLOAD BAY DOORS	1,700	SANDWICH
VERTICAL STABILIZER	1,000	SKIN/STIFFENER
ELEVONS	1,070	SKIN/STIFFENER SANDWICH
BORON/ALUMINUM		
THRUST STRUCTURE	1,270	TUBULAR
MAIN LANDING GEAR DRAG BRACE	150	TUBULAR

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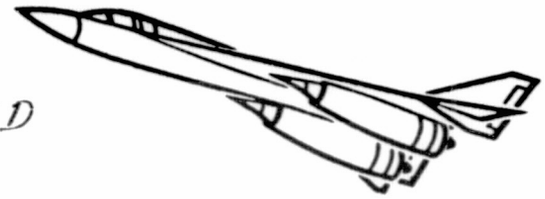
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MCDONNELL DOUGLAS PRESENTATION



HITAC

(HIGH TEMPERATURE ADVANCED COMPOSITES)



POLYIMIDE COMPOSITES DEVELOPMENT

AF CONTRACT F33615-70-C-1546

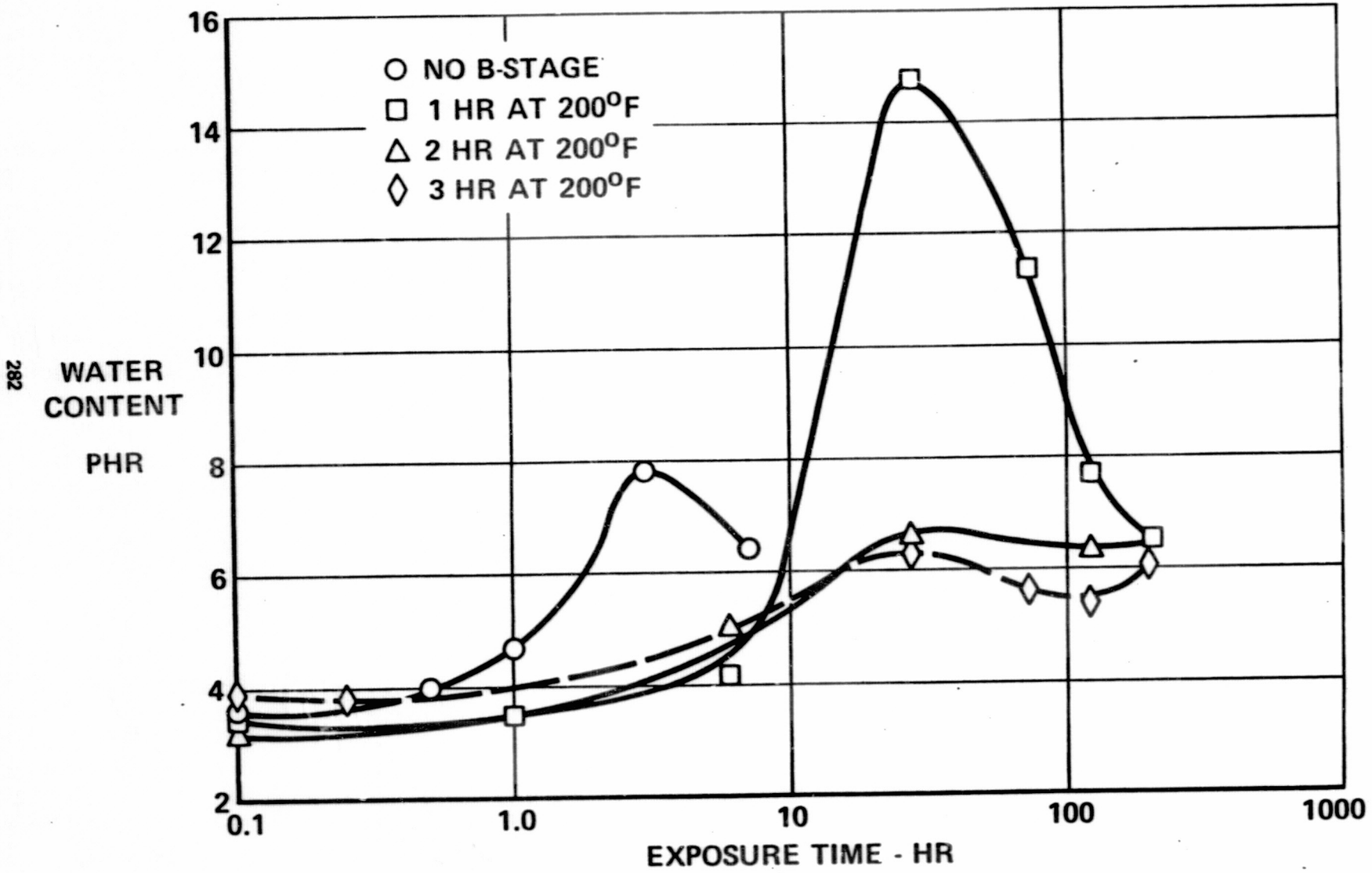
HITAC PROGRAM SCOPE

- MATERIALS DEVELOPMENT
- F-4 RUDDER FABRICATION AND TEST
- DESIGN ALLOWABLES TO 550°F
- F-15 WING COMPRESSION PANEL FABRICATION AND TEST

GP75 0226 10

POLYIMIDE PREPREG

WATER CONTENT vs TIME



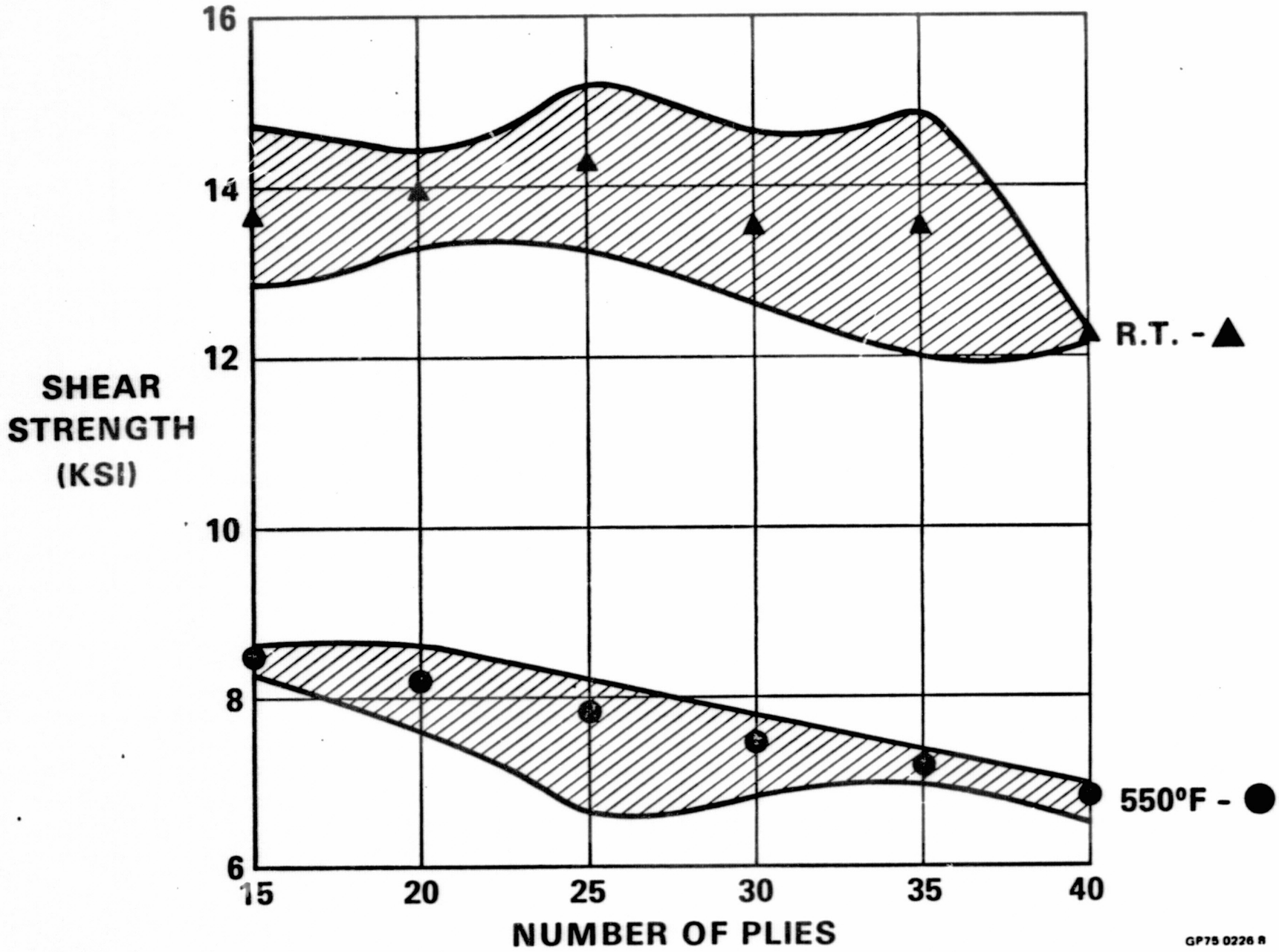
GP71-0428-43

PREPREG GAS ANALYSIS

TEST ITEM	LAMINATE DATE				
	1-28 -2	2-18 -26	2-18 -28	3-10 -97	3-10 -98
RESIN SOLIDS %	26.9	26.3	29.5	23.7	24.1
RESIN VOLAT. %	30.1	21.2	21.4	28.1	27.5
PREPREG VOLAT %	10.3	7.2	8.0	8.4	8.4
NMP-% VOLAT.	61.0	60.4	51.2	53.2	60.8
ETHAN. - % VOLAT.	26.3	26.6	26.4	26.2	27.8
WATER - % VOLAT.	12.7	13.0	22.4	20.6	11.4
PANEL DELAM.	YES	NO	YES	YES	NO

GP71-0428-51

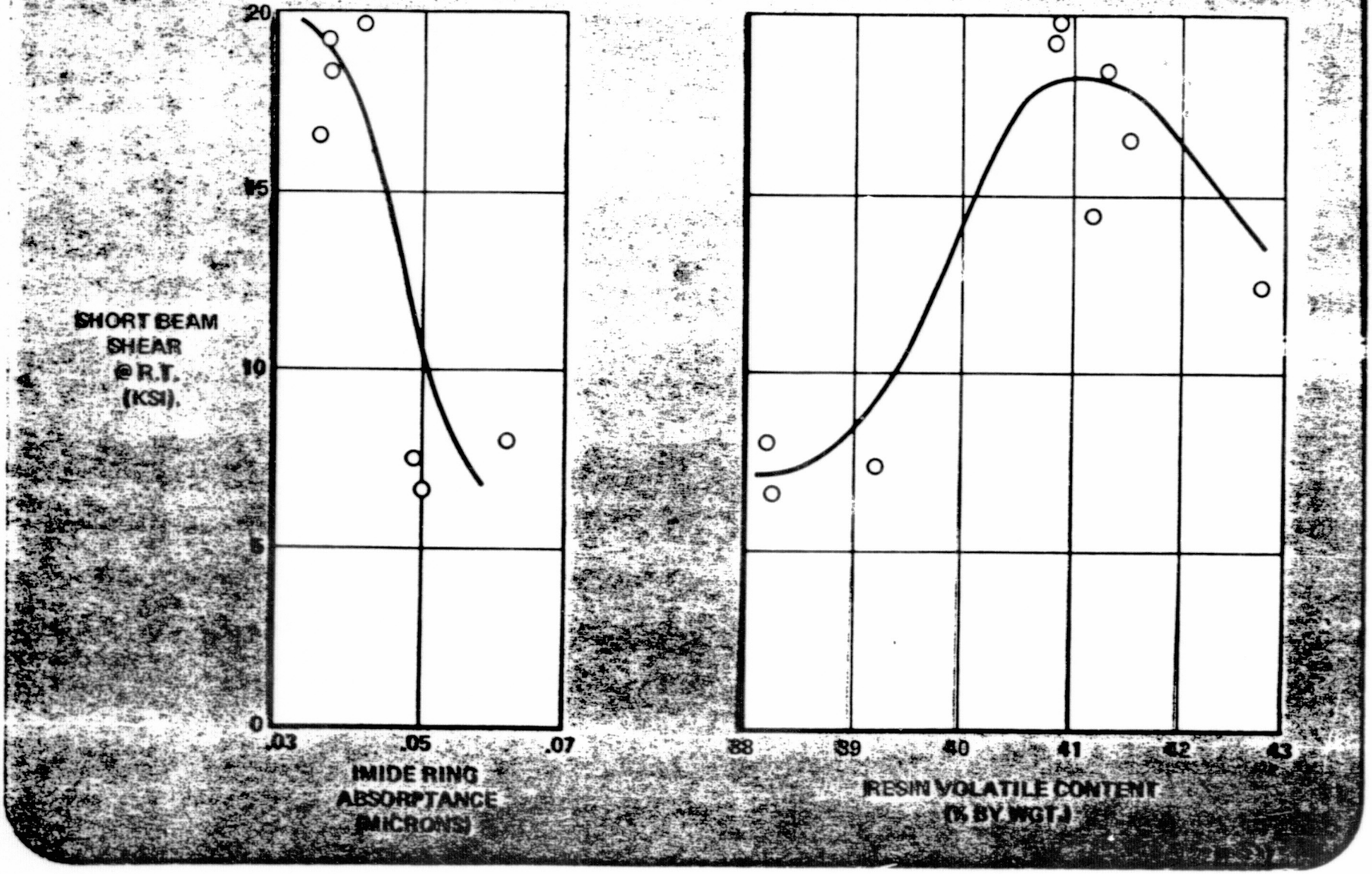
BORON/POLYIMIDE - STRENGTH vs TEMPERATURE



GP75 0226 R

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OF POOR QUALITY

B/SB703 COMPOSITE PREPREG ANALYSIS



BORON/SKYBOND 703 DESIGN ALLOWABLES

PROPERTY	TEST TEMP (^{0}F)	TIME @ TEMP (HR)	FAILURE STRESS (PSI)	FAILURE STRAIN (μ IN./IN.)	ELASTIC MODULUS (MSI)
0^0 TENSION	RT	–	203,900	7,420	32.2
	550	1/2	107,600	4,690	28.0
	550	100	108,200	5,000	32.7
0^0 COMPRESSION	RT	–	226,200	–	32.7
	550	1/2	107,000	–	29.3
90^0 TENSION	RT	–	–	3,014	2.45
	550	1/2	–	7,400	1.68
	550	100	–	7,940	1.56
$\pm 45^0$ IN-PLANE SHEAR	RT	–	59,250	10,750	7.94
	550	1/2	42,930	10,080	7.5
$0\text{-}90^0$ IN-PLANE SHEAR	RT	–	9,350	57,190	0.9
	550	1/2	5,940	247,400	0.4
$\pm 45, 0_2, 90$ TENSION	RT	–	119,000	8,090	16.0
$\pm 45, 0_2, 90$ COMPRESSION	RT	–	187,000	12,080	16.5

GP75 0226 1

MODMOR II/SKYBOND 703 DESIGN ALLOWABLES

PROPERTY	TEST TEMP (^{0}F)	TIME @ TEMP (HR)	FAILURE STRESS (PSI)	FAILURE STRAIN (μ IN./IN.)	ELASTIC MODULUS (MSI)
0^0 TENSION	RT	–	193,800	8,692	23.2
	550	1/2	156,000	7,429	23.6
	550	100	144,700	7,867	20.7
0^0 COMPRESSION	RT	–	144,900	9,034	22.0
	550	1/2	55,500*		
	550	100	38,900*		
90^0 TENSION	RT	–	–	4,535	2.02
	550	1/2	–	5,000	1.15
	550	100	–	4,708	1.20
$\pm 45^0$ IN-PLANE SHEAR	RT	–	38,500	11,600	6.4
	550	1/2	21,500	–	–
0-90 IN-PLANE SHEAR	RT	–	7,800	35,400	0.7
	550	1/2	4,910	37,500	0.4
$\pm 45, 0_2, 90$ TENSION	RT	–	97,500		
$\pm 45, 0_2, 90$ COMPRESSION	RT	–	69,700		

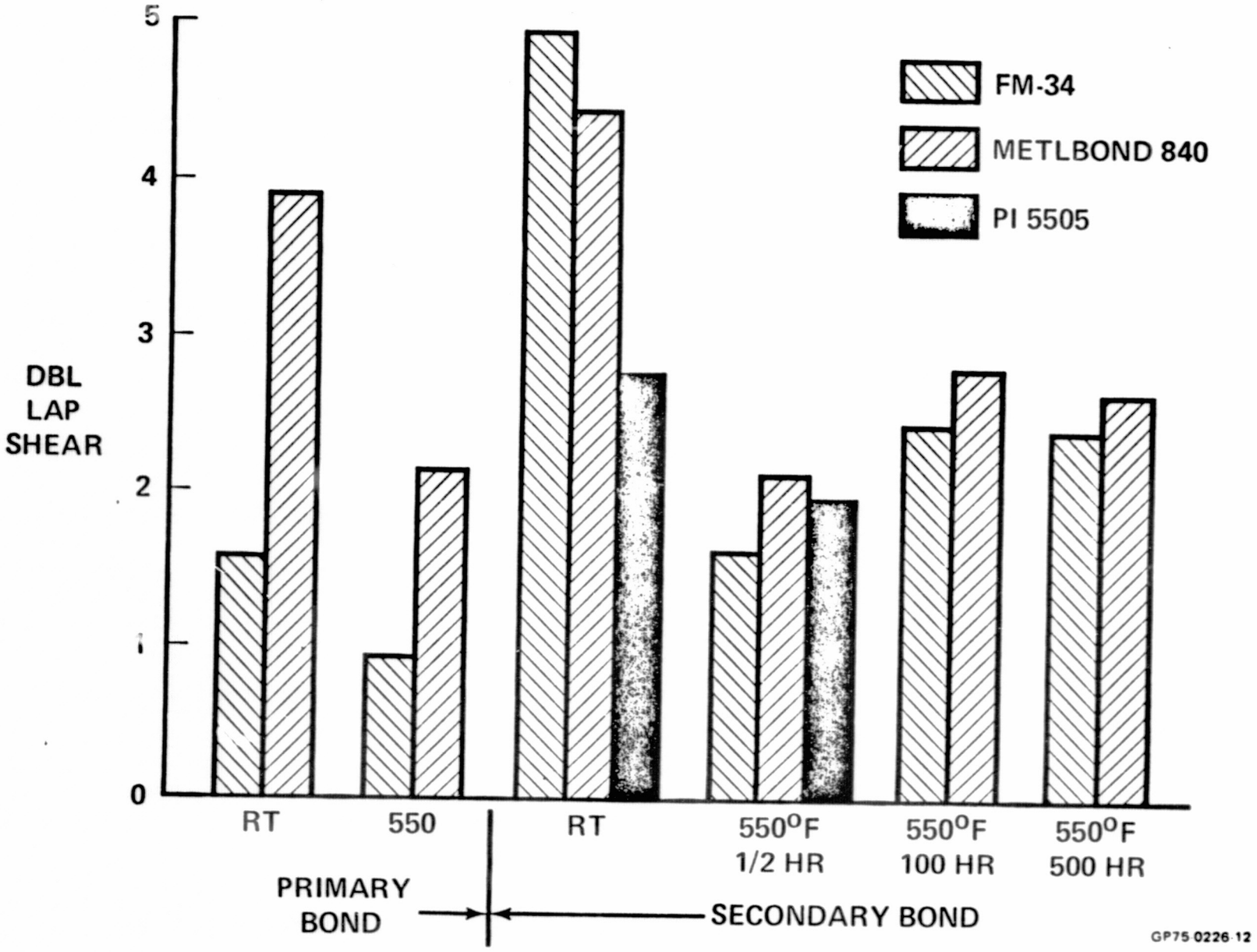
* Edgewise Compression

MATERIAL PROPERTY COMPARISON

MATERIAL	TEST TEMP (^{0}F)	0^0 F_{TU} (KSI)	0^0 F_{cu} (KSI)	0^0 FLEXURE (KSI)	90^0 ϵ_{tu} (μIN./IN.)	S.B. SHEAR (KSI)
BORON/SB703	RT	223	366	270	3010	14.7
	550	128	107	224	7940	8.2
BORON/EPOXY	RT	245	447	270	4460	15.7
GRAPH (II)/SB703	RT	213	178	220	4540	13.0
	550	169	64	130	5000	8.0
AS/SP286	RT	202	247	222	5180	15.1

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POLYIMIDE ADHESIVES



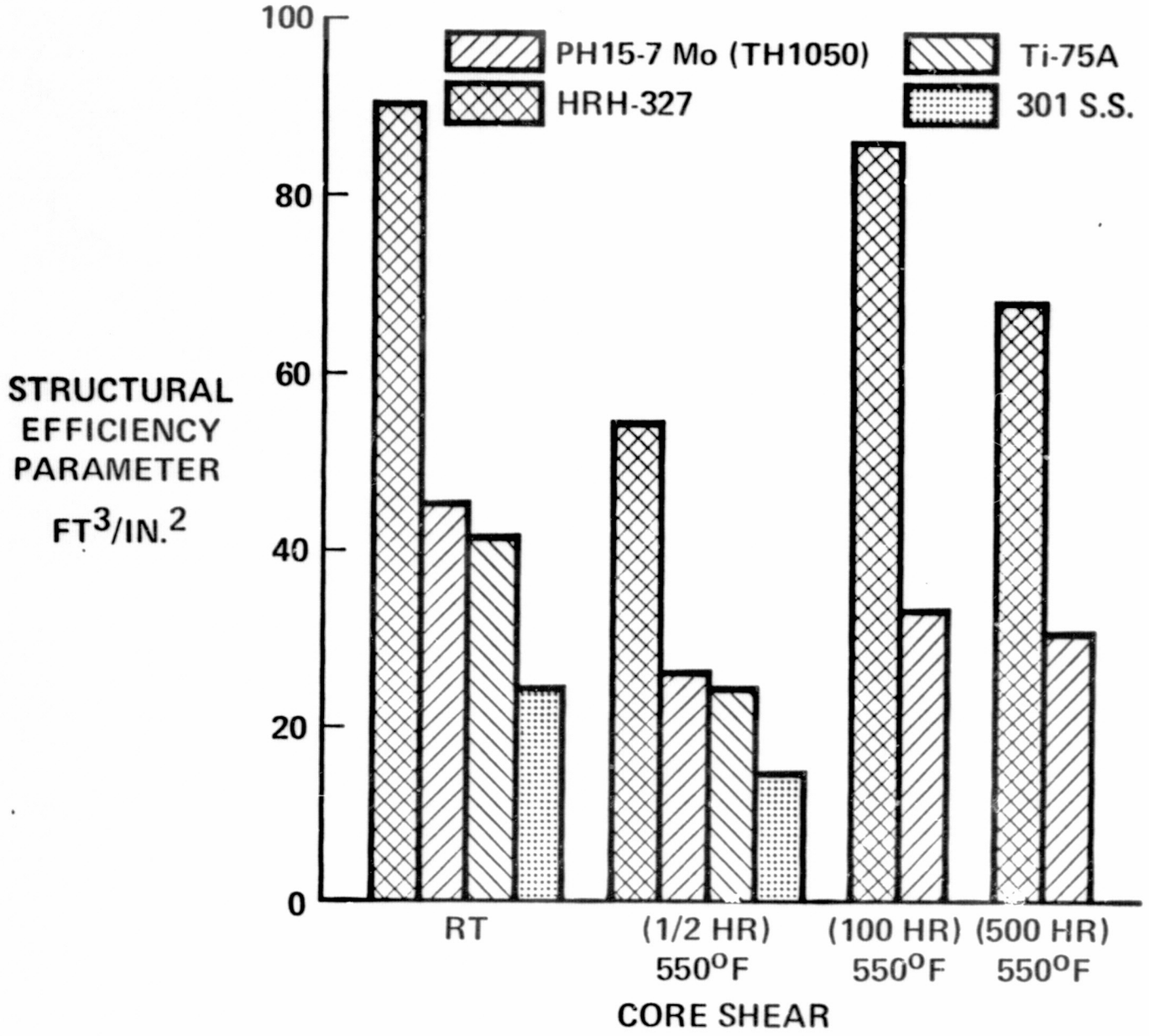
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POLYMIDE ADHESIVE HONEYCOMB FLATWISE TENSION DATA

ADHESIVE SYSTEM	EXPOSURE CONDITION	FLATWISE TENSION (PSI)	
		R.T.	550°F
WRD SB703/SB703	NONE	745	401
PRIMER	500 HRS @ 550°F	318	287
WRD SB703/BR-34	NONE	797	385
PRIMER	500 HRS @ 550°F	427	328
FM-34/BR-34	NONE	568	308
PRIMER	500 HRS @ 550°F	174	275

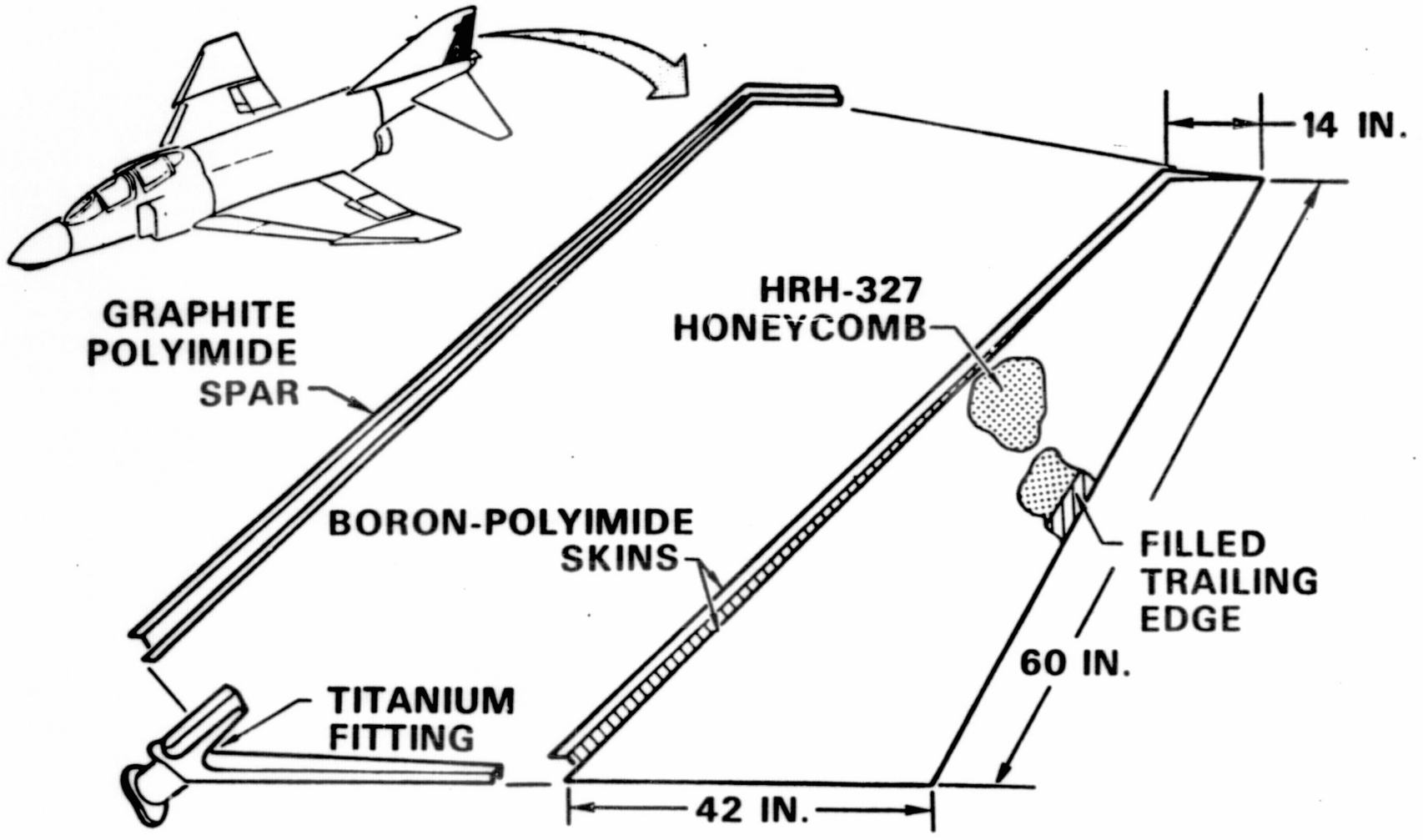
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STRUCTURAL EFFICIENCY COMPARISON OF CANDIDATE HONEYCOMB CORE



GP75 0226 14

F-4 RUDDER COMPONENT

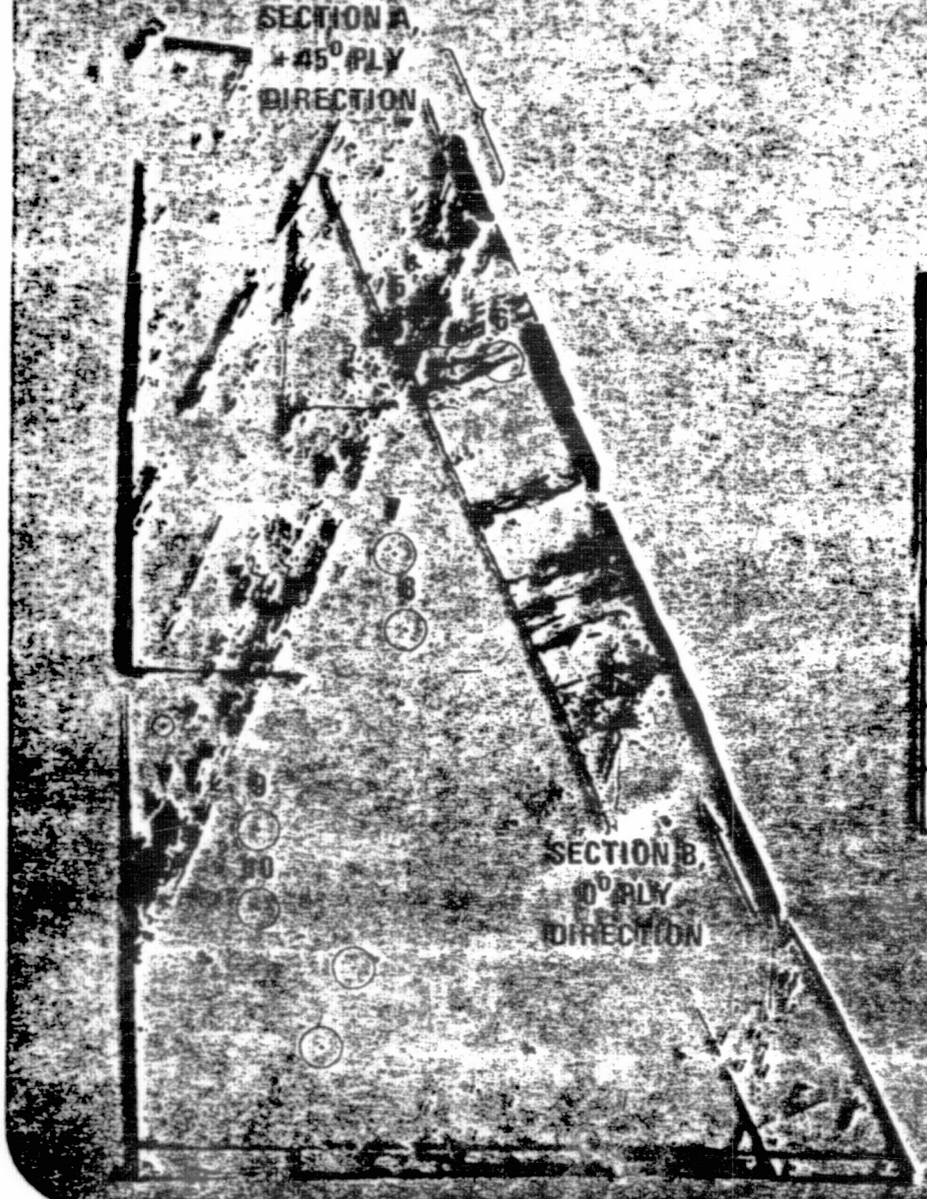


RUDDER SCALE-UP COMPONENT

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C-SCAN OF DELAMINATED BORON POLYIMIDE



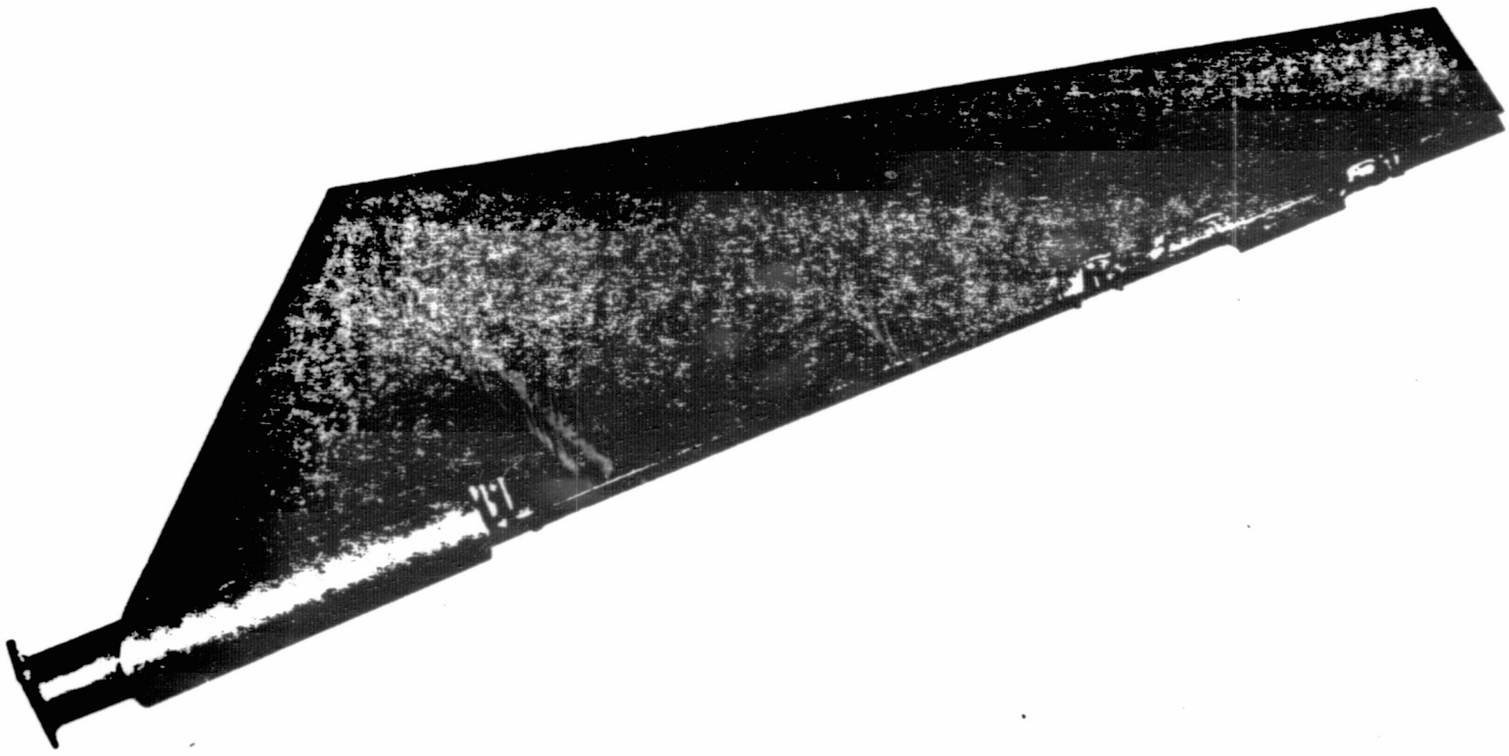
PLUG NO.	% DELAM.	FLATWISE TENSION (PSI)
5	66	395
6	33	685
7	0	1385
8	0	1420
9	0	1040
10	0	1205

RUDDER PROCESS CONTROL TESTS

COMPONENT	PROPERTY	TEST TEMP (^{0}F)	MINIMUM REQUIRED (KSI)	ACTUAL VALUE (KSI)
BORON/SB703 SKINS	0^0 FLEXURE	RT	190.0	270
		550	155.0	224
	S.B. SHEAR	RT	11.0	13.0
		550	6.0	8.1
GRAPH/SB703 SPAR-RIB	0^0 FLEXURE	RT	170.0	199.0
		550	90.0	130.0
	S.B. SHEAR	RT	8.0	13.0
		550	4.5	7.7

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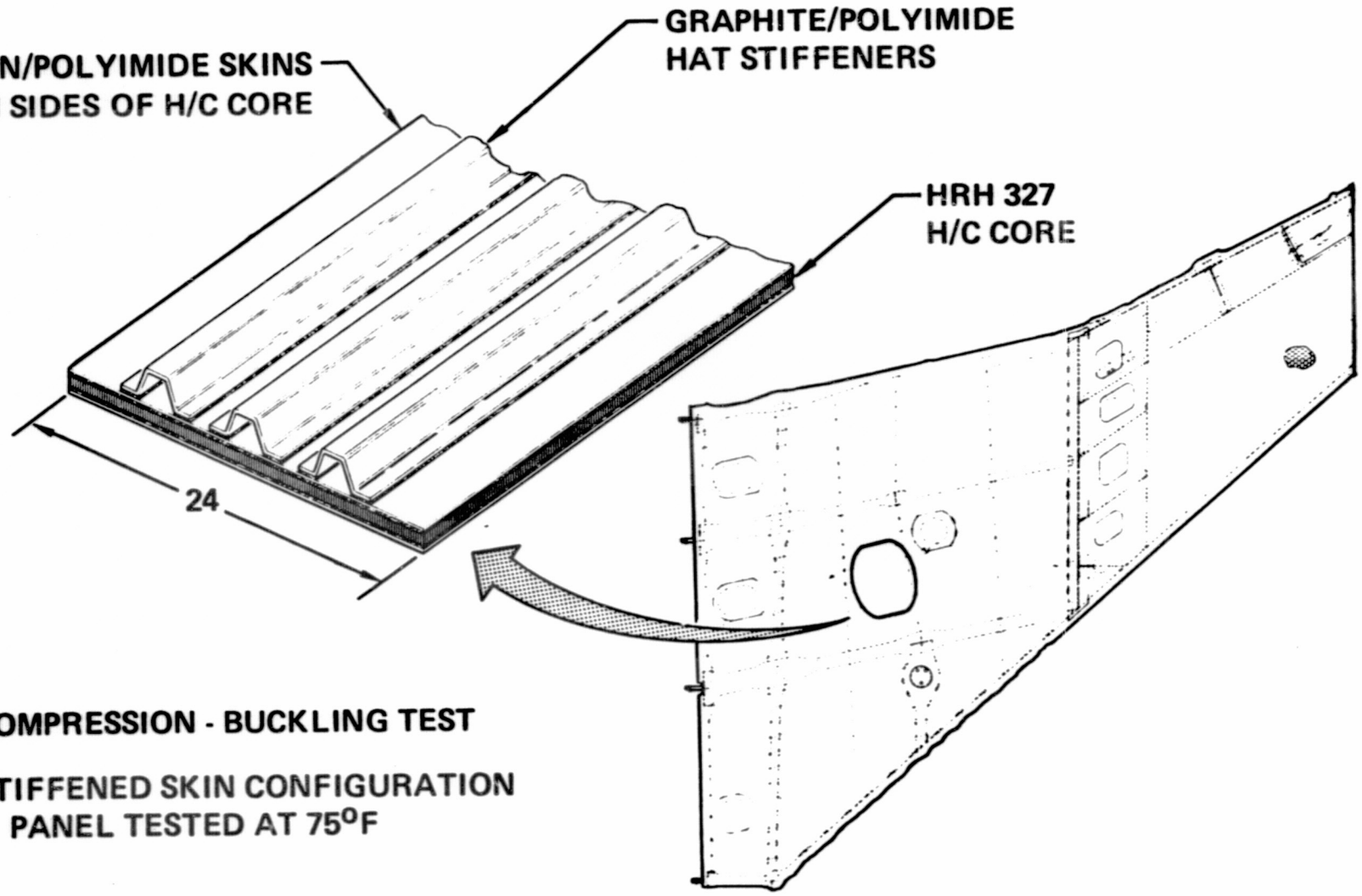
F-4 BORON POLYMIDE RUDDER



295

COMP. NOTES: PROCESSING TECHNOLOGY FOR: Plate No. 204C-86992
B/PI. SKINS

WING TORQUE BOX TEST PANEL



COMPRESSION - BUCKLING TEST

STIFFENED SKIN CONFIGURATION
PANEL TESTED AT 75°F

GP75-0226-7

NEW POLYIMIDE RESIN EVALUATION

PROPERTY	THICKNESS (PLIES)	TEST TEMP (^{0}F)	P105 ADDITION TYPE		SB 703 CONDENSATION TYPE	
			B	G	B	G
S.B. SHEAR (KSI)	15	RT	6.8	10	13-20	11-16
		550	7.3	6	7-10	6-8
		600	6.0	5.7	–	–
	40	RT	7.1	9.5	12-15	–
		550	5.4	5.5	6-9	–
		600	5.8	4.4	–	–
0^0 FLEXURE (KSI)	15	RT	245	148	220-270	170-215
		550	222	107	180-210	120-155
		600	–	102	–	–

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NOTES: CONDENSATION

DIGAP — LONG POST CURE TIME

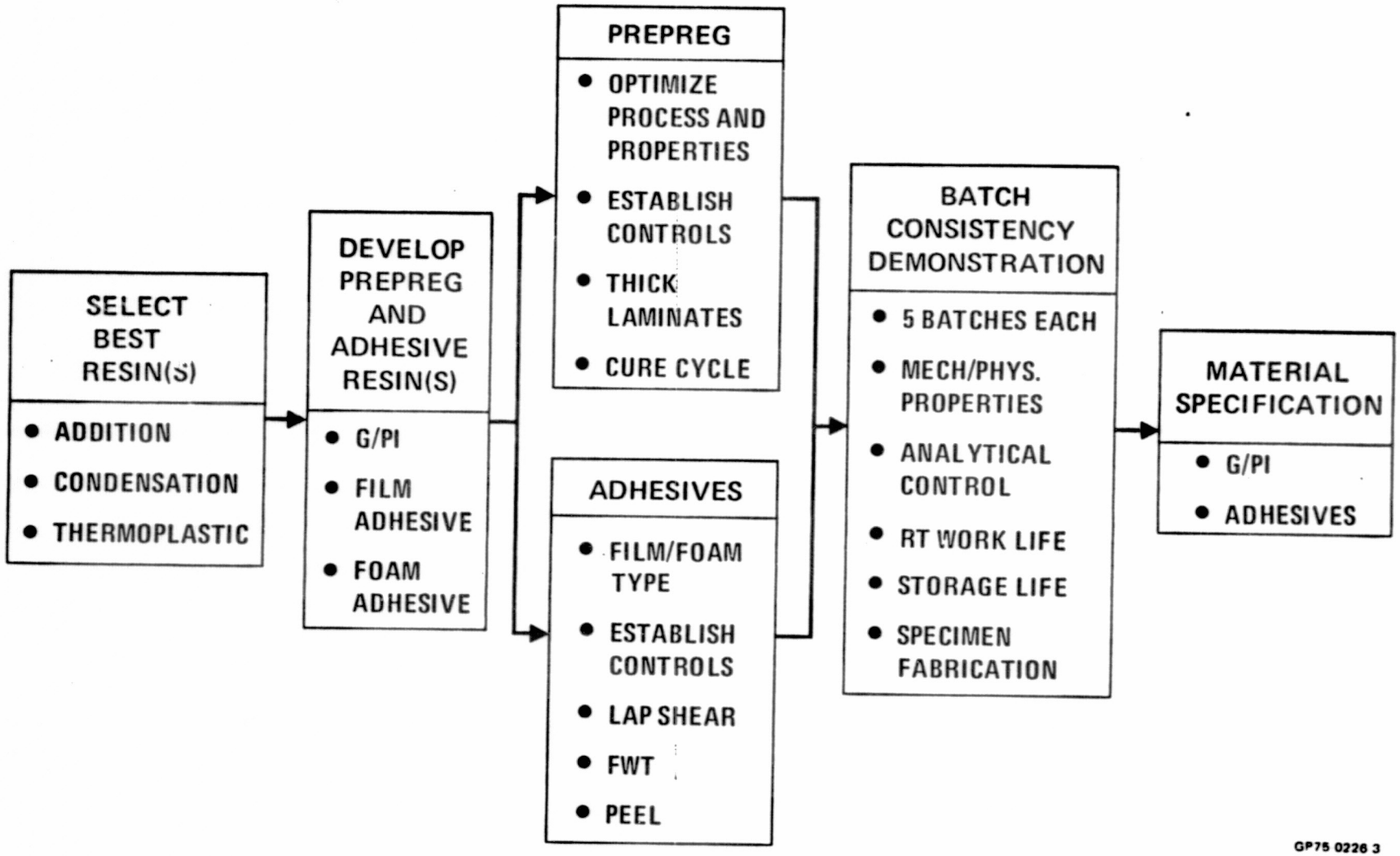
CONCLUSIONS

- PAST PROGRAMS HAVE NOT SHOWN PRODUCTION STATUS
- PROCESSING INCONSISTENCY STILL PROBLEM
- MAJOR PROGRAM NEEDED

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POLYIMIDE ROAD MAP

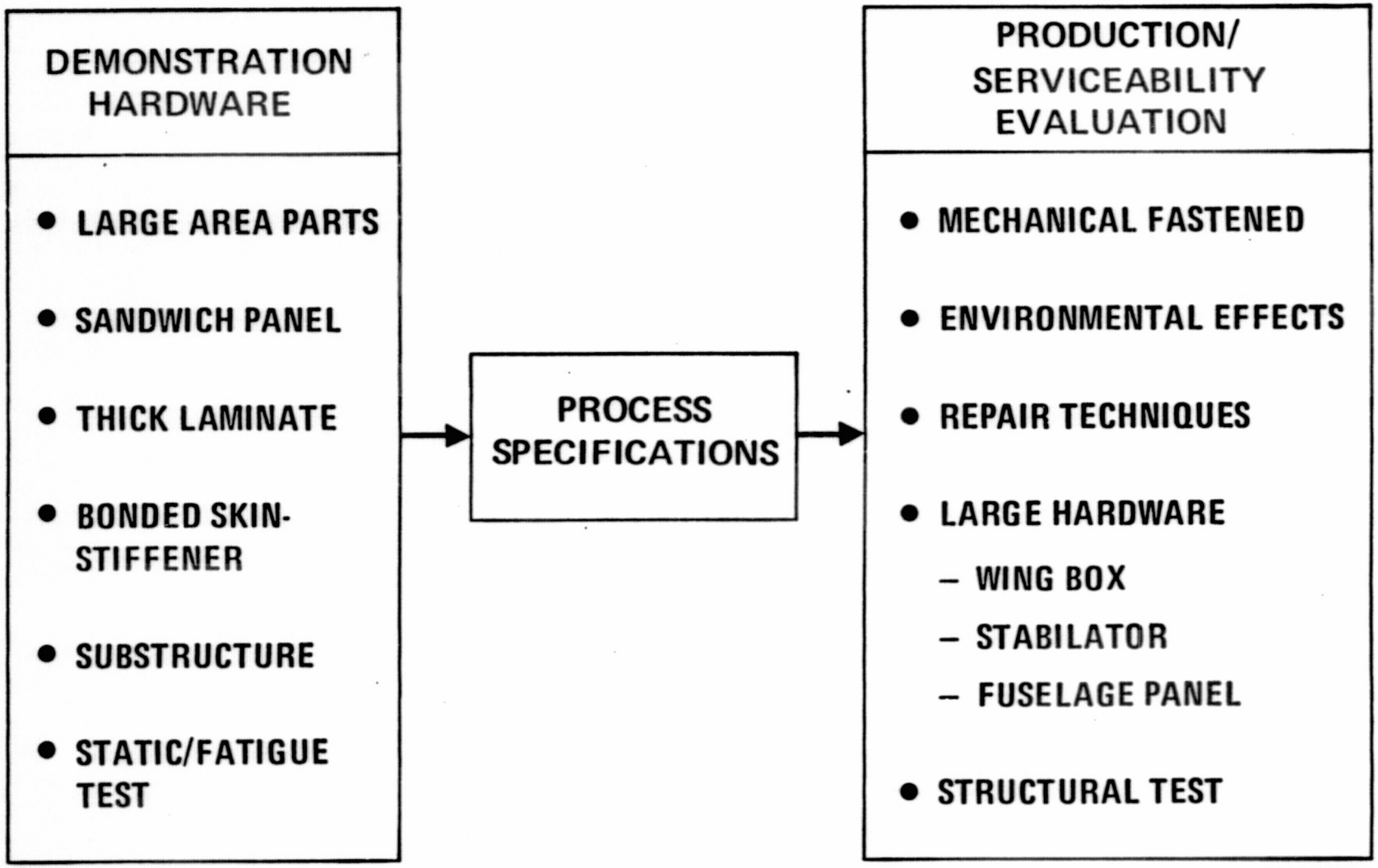
PHASE 1 - MATERIAL DEVELOPMENT



GP75 0226 3

POLYIMIDE ROAD MAP

PHASE 2 - HARDWARE DEVELOPMENT



GP75 0226 4

MONSANTO PRESENTATION

MONSANTO PRESENTATION

MONSANTO POLYIMIDES

PREPARED FOR VERBAL PRESENTATION

AT

NASA CONFERENCE

ON

GRAPHITE/POLYIMIDE COMPOSITE MATERIALS

WILLIAMSBURG, VIRGINIA

MARCH 17-19, 1975

Albert H. Markhart

Monsanto Company

MONSANTO POLYIMIDES

I. INTRODUCTION

Monsanto Company has been selling polyimide precursor solutions, known as Skybond® Resins, for more than 10 years. Initially introduced as high performance electrical insulating varnishes, their utility as laminating resins soon became apparent. The need for improved oxidative resistance at elevated temperatures was emphasized in the expanding aerospace development programs and Skybond Resins were studied for a variety of applications. Glass cloth reinforcement was most widely used for a number of years, followed by quartz, boron and more recently, graphite.

Monsanto sells only the basic polyimide precursor resins, not prepreg or laminated parts. Hence, the application information developed in-house has been limited to relatively small test panels, and was designed to provide starting information for our customers. Prepreggers and fabricators developed their own specific techniques for using Skybond Resins, which were kept confidential. During the past several years, however, a number of publications have described the preparation of composites using Skybond Resins on a variety of substrates.

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In this presentation I will briefly describe the Skybond® Resin product line, take a quick look at the chemistry involved, and present data on composites, emphasizing published information from workers in the field. Finally, a brief discussion of special polyimide products will be made, including an experimental resin, polyimide foams and polyimide microballoons.

II. SKYBOND RESINS

In Table I, the standard and special Skybond products are listed. Note that the reactive solids contents of all but one of the solutions are relatively high, 55-65%, with the viscosities in the range of 3000-4500 cps.; this is in contrast to Skybond 705 where the solids content is 19% and viscosity is ca. 1200 cps. Skybond 705 differs from the others in being of higher molecular weight and thus requiring that it be supplied at the lower concentration. This resin is preferred for coating and sealing applications, whereas the others are recommended as composite matrix resins.

Skybond Resins 700, 705, and 709 give composites of essentially the same high level of oxidative-thermal resistance, whereas Skybond 703 has been modified to provide

improved processability at a slight loss in oxidative stability. Skybond® 709 is a "controlled flow" resin as is Skybond 710, which shows dramatically improved life in glass composites and has been studied extensively with graphite. Data emphasizing these points will be given as applications are discussed.

The Skybond Resins listed can be supplied in drum or bulk quantities with raw materials offering no foreseeable availability problems. The products are manufactured in standard production units by well-defined processes which have been readily scaled up when necessary.

Special products include, in addition to the Skybond 710, RI-7271-01 foamable powder - to be discussed below - and various resin modifications made for specific customer requirements which need not be detailed here.

III. SKYBOND CHEMISTRY

In Figure 1 the very familiar reaction of a dianhydride and a diamine is shown, first forming a soluble polyamide polymer which can subsequently be converted *in situ* to the polyimide structure. The pioneering products of DuPont which utilized this chemistry employed pyromellitic dianhydride,

with Monsanto subsequently recognizing the value of the benzophenone dianhydride (BTDA). Skybond® 705, the higher molecular weight product mentioned earlier, is basically of this type.

The importance of BTDA was emphasized when Monsanto made a major contribution to this field by discovery of the "monomer approach" to polyimide resins, as shown in Figure 2. In this method, the dianhydride is converted to the bis (half-ester) before contact is made with the amine. The reactivity of the diester is of course much lower than the anhydride itself and polymerization can thus be delayed until actual application. High solids varnishes at a relatively low viscosity are thus feasible. All of the solution products in Table I except Skybond 705 are of this general type and all thus require in situ polyimide formation with consequent removal of water and alcohol as volatiles in addition to solvents. As suggested above, BTDA is uniquely qualified to perform well in the "monomer approach", offering a processible system combined with maximum oxidative stability compared to other commercially available dianhydrides.

In recent years the monomer approach to polyimides has been adopted by a number of other workers, using various alcohols (including glycols) and various mono- and di-anhydrides.

Emphasis throughout Skybond® Resin development has been on thermal stability. The TGA curve of Figure 3 shows that cured Skybond Resin 700 undergoes very little weight loss up to 500°C. (932°F.) even in an air atmosphere. A similar set of curves in Figure 4 for cured Skybond 703 shows weight loss begins at a somewhat lower temperature but loss levels out at the same point as Skybond 700 in an inert atmosphere. This small loss in thermal stability is accompanied, however, by processing advantages referred to above. Long-term isothermal weight loss studies confirm the oxidative stability of these materials and data of this type will be shown later in connection with an experimental resin.

IV. GLASS COMPOSITES

Most of our laboratory composite evaluation work has been done on glass substrates and I will briefly mention a

few observations from this work which may be of importance to graphite fiber composites as well.

To determine the thermal oxidative stability of Skybond® 700 glass laminates, a series of specimens were prepared from 12-ply 181-A1100 prepreg and aged in circulating air at four temperatures, 550°, 600°, 700° and 800°F. These specific laminates were prepared from prepreg which had been B-staged at 275°F. to a resin solids of 42-44%, a volatile content of 8-8.5% and a flow of 11-13%. Lamination in this early work was done at 600°F. and 250 psi. The results of this aging study are shown in Figure 5. If 20,000 psi flexural strength is taken as an end point, the laminate life would be considered to be approximately 10 hours at 800°, 100 hours at 700°, 1000 hours at 600° and 10,000 hours at 550°F.

Another aspect of our work with glass as a substrate which could also be of interest in graphite work, is the variability of the substrate both in the nature of the glass surface and in the nature of the glass itself. Let us first consider the glass surface.

Great difficulty was experienced initially in making reproducible laminates from different bolts of presumably

the same type of cloth. Initial strength and aging were affected. Study of the prepregging step showed that the ability of the cloth to be wet by the impregnating solution varied greatly and in general varied with the "hand" or drape of the cloth. Soft-drape cloth would wet readily, hard-drape cloth poorly. This is demonstrated in Slide 1, which shows two transparent cylinders containing a Skybond varnish and samples of hard- and soft-drape cloth. The soft-drape cloth on the right has permitted penetration of the dark solution whereas the hard-drape has resisted being wet by the varnish. Slides 2 and 3 show closeup views of this effect. Only soft-drape cloth gave laminates of maximum thermal stability. Glass cloth manufacturers were very helpful in discussion of the variables affecting the surface of the cloth, such as residual glycerine, level and degree of cross-linking of the A-1100 finish, etc.

The other substrate variable of great significance was the high temperature aging characteristics of the glass itself. We had rather naively assumed that the change in our organic resin at high temperatures would far outweigh any change in the inorganic glass. This was the case with certain bolts of cloth but not with others. The effect of

temperature on glass can be readily shown by merely holding the cloth at 700°F. for 100 hours. A heat-sensitive glass becomes brittle and weak; a stable glass remains flexible and strong. Samples of aged glass of the two types have been brought for you to examine. Much more could be said about glass composites, but we must turn our attention to graphite/polyimide systems. Suffice it to say that many, many articles have been successfully made with Skybond/glass combinations.

V. GRAPHITE COMPOSITES

As was indicated at the start of this discussion, most of the work done on graphite-Skybond® composites has been done by fabricators rather than by ourselves, but enough has been published to show the potential of this system. Since much of the reported work has been done with Skybond Resin 710, a brief comment on this product is in order.

Skybond 710 was developed to provide still greater oxidative thermal stability on glass than was available from the other Skybond resins. That this was accomplished is shown by Figure 6 which describes an accelerated flex aging study on glass of Skybond 710 vs. Skybond 700. The lower initial strength of the newer resin is shown, but its very

flat aging curve indicates that after about 100 hours its strength surpasses that of the Skybond® 700 laminate. (Incidentally, the graph also shows the effect of hard vs. soft-drape glass cloth.) To provide visual impact of this experiment, some of the samples which were actually tested have been brought along and are mounted on this card for you to examine. An Electrofax copy of the display board is included in your charts as Figure 7.

This resin, Skybond 710, was chosen over two other polyimide types by Jon Poesch[1] of Hercules, Inc. for the development of lightweight graphite/polyimide sandwich panels. Hercules HT-S fiber/Skybond 710 face sheets were prepared from prepreg containing 20-25% solvent in a vacuum bag lay-up with ample bleeder material to maximize volatile removal and avoid premature resin precipitation. A step cure with holds at 175°, 250° and 350°F. and 100 psi was used. Excellent test laminates were fabricated using 2, 3, 5, 6 and 9 plies of prepreg. Laminate panel properties are listed in Table II. Core fabrication is summarized in Table III and the sandwich panel construction described in Table IV. A liquid adhesive was used in this case to avoid

the excess weight of a scrim cloth in this very lightweight composite. More will be said later concerning the Monsanto reinforcing foam RI-7271. Table V lists the properties of the completed honeycomb panel, showing the high strength retention at 500°F. and finally, Table VI compares the graphite/Skybond® 710 honeycomb with similar honeycombs of aluminum, glass/polyimide and Nomex. It can be seen that the Skybond 710 product is superior in every property at elevated temperatures with the exception of compressive modulus where aluminum is somewhat superior. In summary, "the manufacture of lightweight carbon fiber honeycomb and sandwich panels was accomplished using standard fiberglass technology without difficulty."

Browning and Marshall[2] have reported on polyimide composites using ozone-treated Thornel with both Skybond 700 and an addition-cured polyimide. After advancement, both types of prepreg tapes were laid up and cured in the same manner. The comparable room temperature properties of post-cured panels are shown in Table VII. Ozone treatment had been found superior to several other methods of surface modification.

Flex aging at 600°F. is shown in Figure 8, pointing

out the slow drop in strength up to 500 hours. Included in this graph are data obtained using S-glass roving as substrate. Although the aging curve is again very flat, showing the high stability of the resin matrix, notice the great drop in strength during the first 1/2 hour of aging - from 108,000 psi to 56,000 psi. A similar drop occurred with the addition polyimide on the S-glass. This again points to the importance of the thermal stability of the substrate finish. In summary, "The best isothermal heat-aging data were obtained with Skybond® 700 and ozone treated Thornel 50 composites. These materials showed no short-term loss of flexural strength and demonstrated a 76% retention of the initial room temperature flexural strength after 500 hours at 600°F."[2]

The effect of surface treatment of graphite fiber was included in the comprehensive study reported by Pike and Maynard.[3] Mechanical properties comparable to epoxy/graphite were obtained from polyimide reinforced with treated HMG-50 fiber. Figure 9 shows the importance of the treatment and also shows the differences found in this particular case between Skybond 700 (15% drop) and Skybond 703 (25% drop), along with an addition polyimide (also 25% drop).

Another comparison of Skybond® 700 and Skybond 703 which measured change in short beam shear strength with temperature is shown in Figure 10. The expected generally higher level of Skybond 700 is apparent, but it should be pointed out that the drop from 600°F. and 700°F. would not be expected and is probably due to incomplete post-cure. For maximum high temperature strength retention, post-cure to the maximum use temperature is strongly recommended.

In this work, a volatile content of 7-8 weight percent prior to molding was optimum. The desolvation step with Skybond Resins was done under vacuum to avoid premature imidization, eliminate air pockets and facilitate resin penetration. Void content varied from less than 1.5% to 10-15%, depending upon desolvation and molding parameters. The effect of void content on short beam shear strength was similar to that reported by Petker for boron/polyimide composites.

J. K. Fincke[4] of the New Enterprise Div. of Monsanto has reported on HMG-50 composites using Skybond 703 and an addition polyimide. Figure 11 shows comparable shear strength properties for the two systems up to 600°F. Long term aging at 600°F., however, shows a significant differ-

ence in 600°F. shear strength retention as indicated by Figure 12. A similar trend for flexural strength is shown in Figure 13. Exposure at 160°F. to jet fuel and Skydrol® 500B hydraulic fuel gave no loss in shear strength.

General Dynamics[5] has reported on an in-depth study of a graphite (HT-S)/polyimide system. With Bill Scheck here in person, I'll merely point out a few items from his report summary. Skybond® Resin 710 was selected and processing techniques developed based on resin characterization and empirical studies. These processing techniques were proven to be completely applicable to producing large complicated parts by the fabrication of several demonstration articles up to 2 inches thick. Successful test results obtained on skin-stringer components can be reliably designed and analyzed much like graphite/epoxy composites.

Studies of the ablation characteristics of Skybond 700 were reported by Juneau[6], using carbon and silica fiber composites. The ability of the polyimide to retain useful mechanical properties at transient temperatures up to 1000°F. makes them of interest in this type of application. The

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ablation characteristics were comparable to phenolic-bonded materials in rocket exhaust environments. Included in the study was an analysis of resin degradation products under vacuum, which included CO and CO_2 as major products, and amines, amides, nitriles, ethers and aromatic ketones.

In connection with polyimide degradation products, the report by Scala[7] et al, on the long-term oxidation of aromatic amide and imide resins at 200-300°C. showed that no HCN was evolved at any temperature or aging time, the main degradation product being CO_2.

VI. EXPERIMENTAL RESIN SYSTEM

Although current Skybond® Resins provide polyimides of very high oxidative thermal stability, a polyimide resin system showing even greater life has been prepared in the laboratory. In contrast to some exotic polymers based on unavailable raw materials which require a complicated series of reactions to prepare, this modified Skybond Resin system is made from available raw materials. The resistance to long-term oxidative weight loss at 700°F. is shown in Figure 14. For the first week or so, weight loss parallels that of Skybond 700 and 709. Thereafter, however, the

experimental product loses weight much more slowly. Composite property information is not yet sufficiently complete to discuss at this time.

VII. POLYIMIDE FOAM

I would like to take just a moment to say a word about a polyimide foam product, RI-7271-01. This product was mentioned, you may recall, in the discussion of honeycomb panels prepared by Hercules and is under active study by other groups. In honeycomb, it was used as a reinforcing material. The cured foam shows the same basic resistance to oxidation as Skybond® 700 and also can be made from readily available raw materials. Much could be said about this material but in the interest of time, let me merely flip through a series of slides which will describe the unusual nature of this product better and faster than words:

Slide	4	Low Density Foam
"	5	Cell Structure
"	6	Smoke Test Chamber
"	7	Smoke Test Samples
"	8	Smoke Test Results

Slide 9	Polyimide Foam/Urethane Foam Composite
" 10	Honeycomb
" 11	Honeycomb & Prepreg Skin
Slides 12-19	M.R.C. Foam Slides
" 20,21	Microballoons

VIII. SUMMARY

In summary, the Skybond® Resin product line has been described, a brief look taken at the chemistry involved, and a summary of some application studies presented. In addition, specialty polyimide products were discussed, including an experimental resin and polyimide foam powder.

IX. REFERENCES

See attached sheet.

TABLE I

SKYBOND® RESINS

Product	Solids %	Brookfield Viscosity cps.	Specific Gravity	pH	Solvent
SKYBOND 700	62	4500	1.17	4.4	NMP
" 703	65	4500	1.17	4.4	NMP
" 705	19	1200	1.07	-	NMP Xylene
" 709	55	2500	1.13	4.8	NMP Xylene Ethanol
Special Products					
SKYBOND 710	55	2500	1.12	4.4	NMP Xylene Ethanol
RI-7271-01	100	-	-	-	-
Others					

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TABLE II

LAMINATE PROPERTIES FOR SANDWICH PANEL

HM-S GRAPHITE/SKYBOND® 710

RESIN CONTENT, Wt. %	23.8
DENSITY, lb./in.^{3}	1.41
FLEXURAL STRENGTH, psi	
70°F.	100,320
600°F.	114,360
FLEXURAL MODULUS, psi x 10^{-6}	
77°F.	17.0
600°F.	20.0
INTERLAMINAR SHEAR, psi	
77°F.	6,650
600°F.	4,650

(J. G. Poesch - Hercules)

TABLE III

CORE FABRICATION

HM-S GRAPHITE/SKYBOND® 710

PREPREG

DRIED 10 min. @ 200 - 250°F.

15 min. @ 250°F. (Vac)

CORRUGATED @ 275°F.

NODE BONDED WITH SKYBOND 703 BASED ADHESIVE

CORE

CURED @ 100 psi to 350°F.

POST-CURED 20 hrs. to 650°F.

(J. G. Poesch - Hercules)

TABLE IV

SANDWICH PANEL CONSTRUCTION

GRAPHITE/SKYBOND® 710

FACE SHEETS	0.011 in. thick
	7 - 0° plies
	2 - 90° plies
CORE	0.9 in. thick
	3/8-in. cell size
CELL EDGE ADHESIVE	Thermadite 17
REINFORCEMENT FOAM	Monsanto RI-7271
FOAM SEALANT	BR-34

(J. G. Poesch - Hercules)

TABLE V

HONEYCOMB PANEL PROPERTIES

GRAPHITE/SKYBOND® 710

PROPERTY	VALUE
TOTAL WEIGHT	.54 psf
FACE SHEET WEIGHT	.16
CORE WEIGHT	.16
ADHESIVE WEIGHT	.10
FOAM WEIGHT	.14

	77°F.	500°F.
FACING STRENGTH, PSI		
Parallel	42,000	31,320
Perpendicular	16,750	17,390
FACING MODULUS, PSI x 10^{-6}		
Parallel	18.0	17.9
Perpendicular	5.1	5.0
FLATWISE SHEAR, PSI		
Parallel	140	110
Perpendicular	80	64
FLATWISE COMP. STR., PSI		
With RI-7271 Foam	>1,000	600
Without Foam	194	150

(J. G. Poesch - Hercules)

TABLE VI

HONEYCOMB PROPERTIES

GRAPHITE/SKYBOND® 710 Vs. ALUMINUM, GLASS/POLYIMIDE, NOMEX

(3/8-in. Cell Size)

Property	Temp. °F.	HM-S Skybond 710	5056 Al	Glass/ PI	Nomex
DENSITY, pcf.		1.94	2.0	2.5	2.0
"L" SHEAR	-150	124	-	-	-
	77	136	140	150	110
	500	110	78	112	-
COMPRESSION	77	194	160	200	150
	500	153	90	150	72
	600	116	-	-	-
COMPRESSION MOD.	77	19,600	45,000	20,000	11,000
	500	19,700	25,200	15,000	5,280
	600	12,600	-	-	-

(J. G. Poesch - Hercules)

TABLE VII

THORNEL/POLYIMIDE COMPOSITES

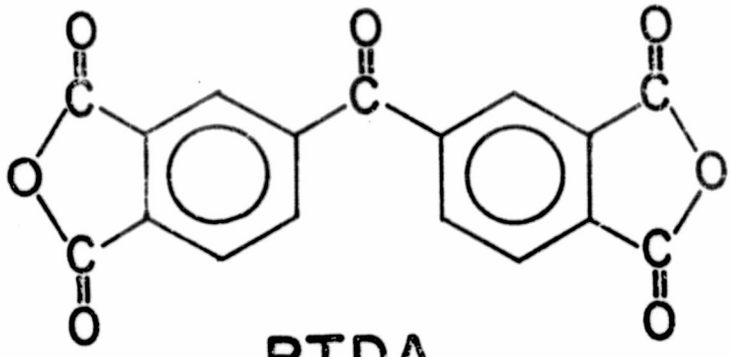
ROOM TEMPERATURE PROPERTIES OF POST-CURED PANELS

	T-50 and ® Skybond 700	T-50 and Addition Polyimide
Flexural Strength ($psi \times 10^{-3}$)	113.8	107.1
Flexural Modulus ($psi \times 10^{-6}$)	14.6	14.9
Short-Beam Shear ($psi \times 10^{-3}$)	5.2	5.2
Density	1.39	1.42
Volume % Fiber	56.2	54.7
Volume % Resin	34.4	32.0
Volume % Voids	9.4	8.3

(C. E. Browning - U. of Dayton)
(J. A. Marshall - AFML)

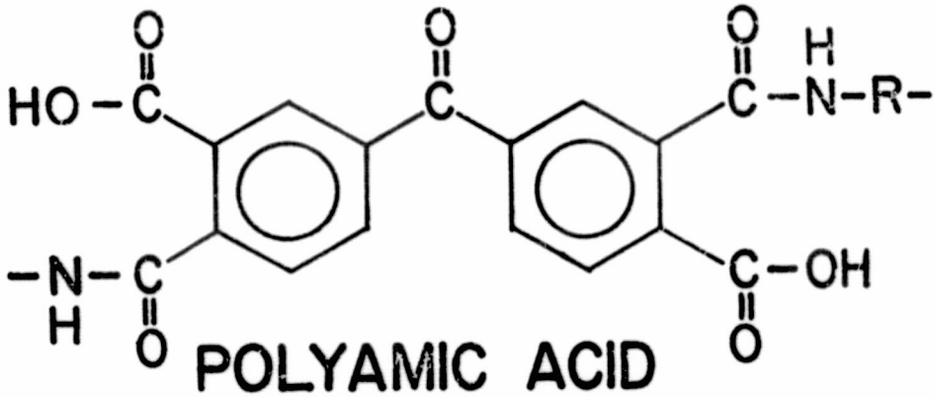
FIG. 1

SKYBOND® RESIN
POLYAMIC ACID TYPE



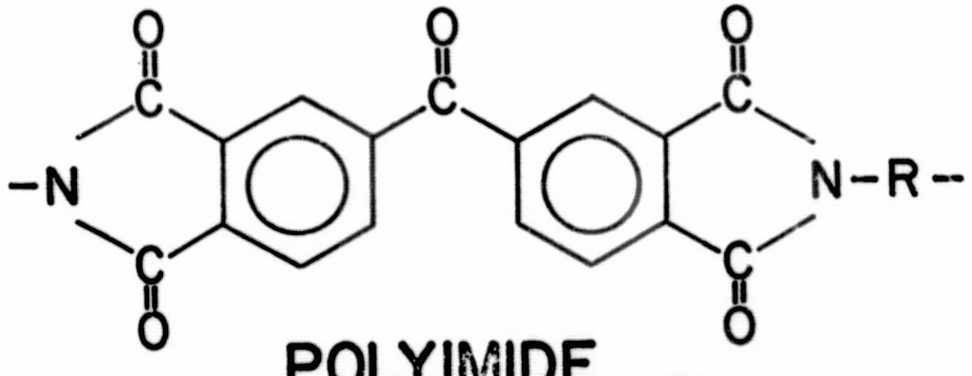
BTDA

$+H_2N-R-NH_2$ ⟶



POLYAMIC ACID

⟶



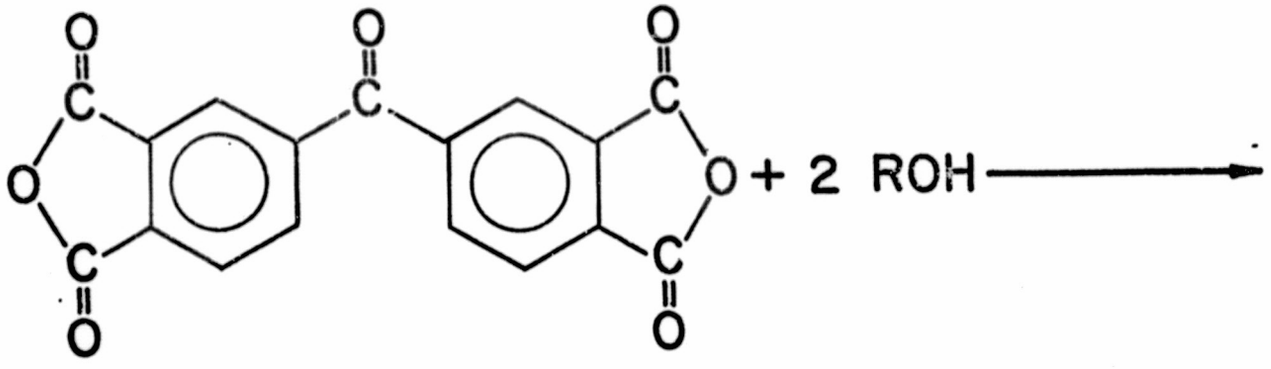
POLYIMIDE

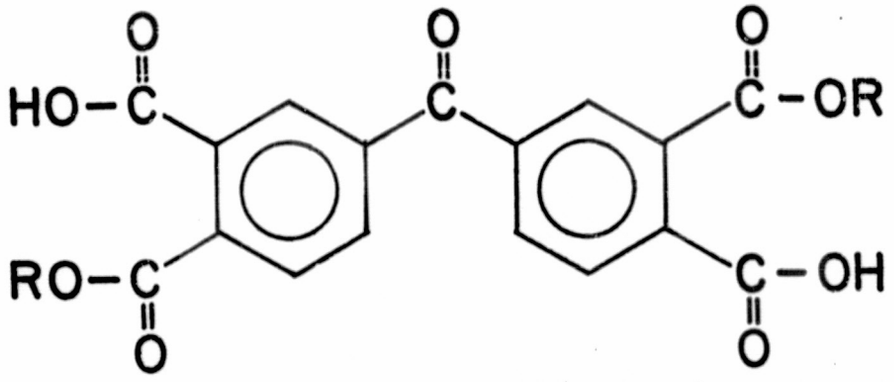
325

U.S. PAT. 3,190,856 (MONSANTO, 1965)

FIG. 2

SKYBOND® RESIN
MONOMER TYPE





bis (HALF-ESTER)

bis (HALF-ESTER) + H_2N-R-NH_2 ⟶

IMPREGNATING VARNISH ⟶

POLYIMIDE

326

U.S. PAT. 3,347,808 (MONSANTO, 1967)

FIG. 3

SAMPLE.	X-AXIS	Y-AXIS	
TGA CURVE SKYBOND® 700 (CURED RESIN)	TEMP. SCALE 100 °C / inch	SCALE 2 mg. / inch	RUN NO.
	SHIFT 0 inch	(SCALE SETTING X 2)	OPERATOR
SIZE 10 mg.	TIME SCALE (ALT.) —	SUPPRESSION 0 mg.	HEATING RATE 20 °C / min. ATM. NITROGEN (35cc/MIN), AIR (0) TIME CONSTANT 1 sec.

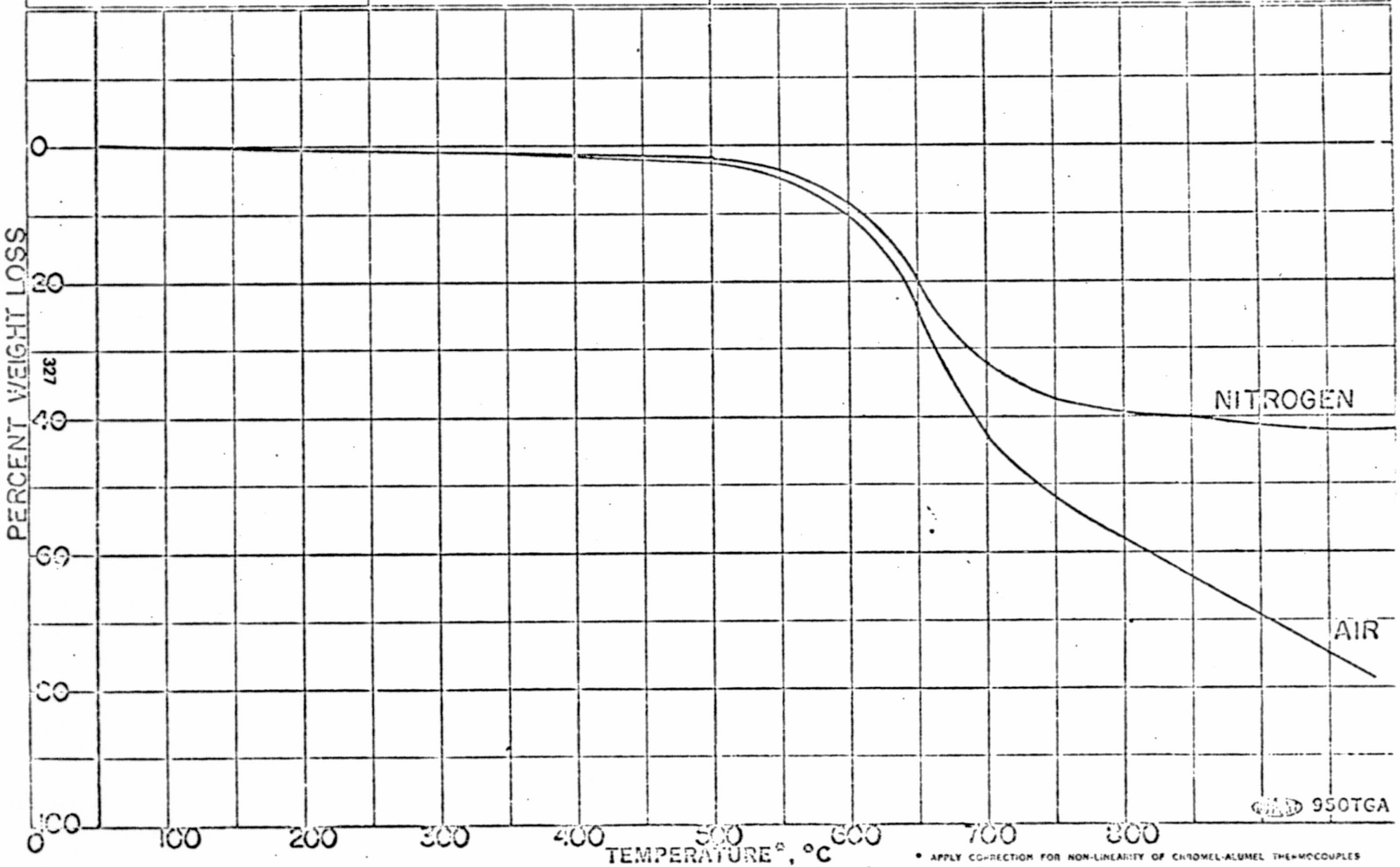
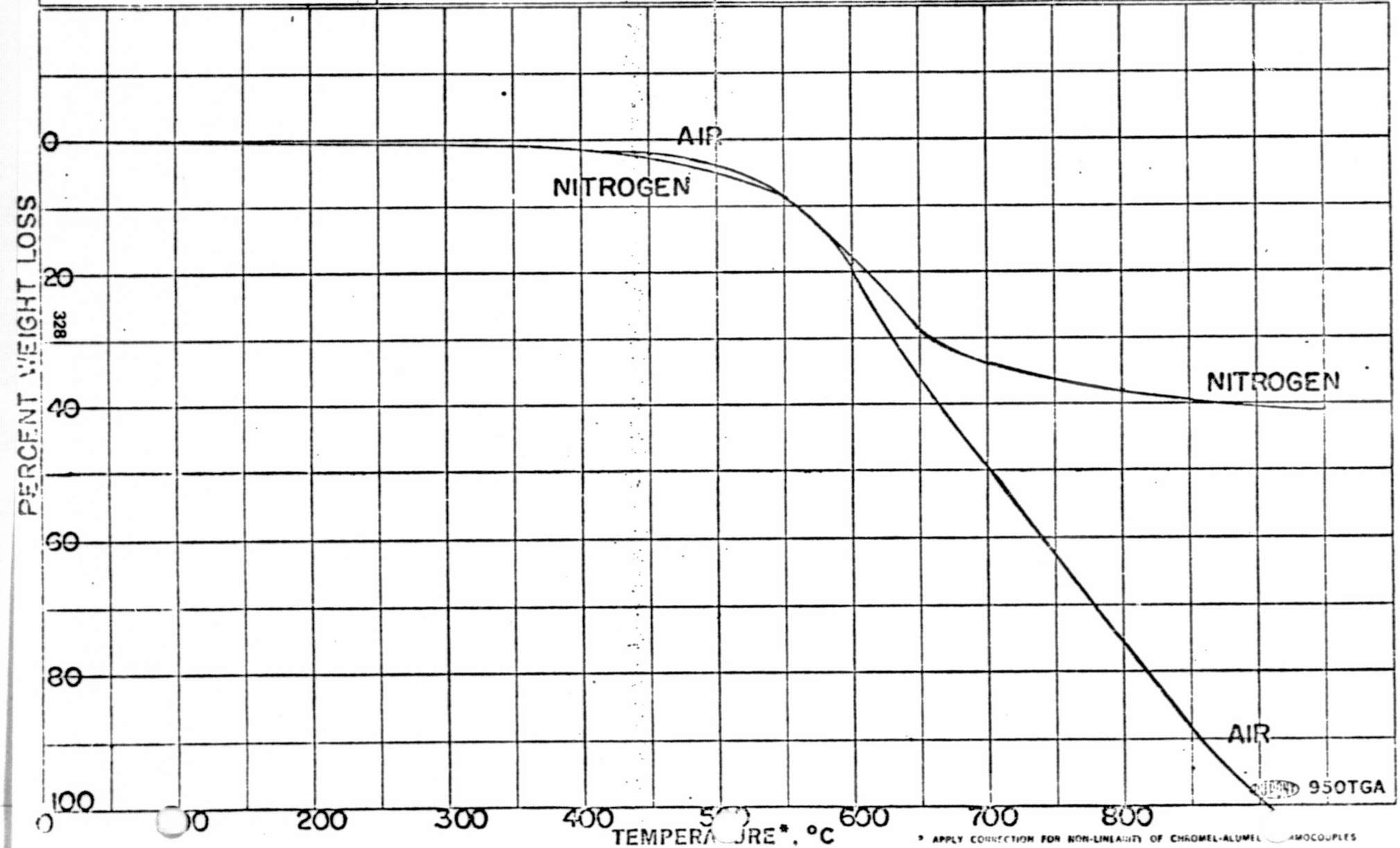


FIG.4

SAMPLE:	X-AXIS	Y-AXIS	
TGA CURVE SKYBOND® 703 (CURED RESIN)	TEMP. SCALE 100 °C / inch	SCALE 2 mg. / inch	RUN NO. ____ DATE ____
	SHIFT 0 inch	(SCALE SETTING X 2)	OPERATOR ____
SIZE 10 mg.	TIME SCALE (ALT.) —	SUPPRESSION 0 mg.	HEATING RATE 20 °C / min.
			ATM. NITROGEN(35cc/MIN), AIR(0)
			TIME CONSTANT 1 sec.



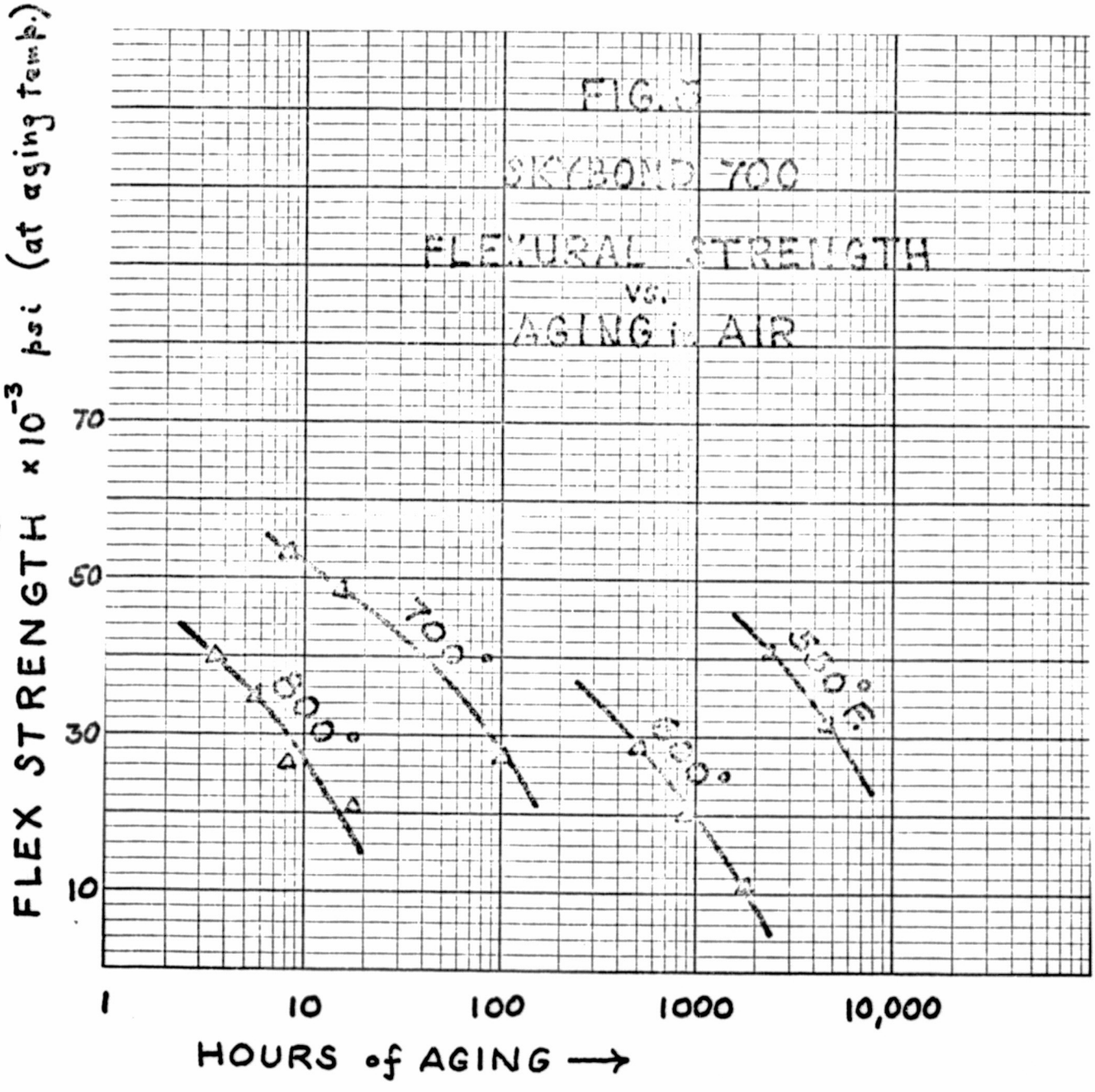

FIG. 3
SKYBOND 700
FLEXURAL STRENGTH
vs.
AGING in AIR
FLEX STRENGTH x10⁻³ psi (at aging temp.)
70
50
30
10
1
10
100
1000
10,000
HOURS of AGING →
700°F.
600°F.
500°F.
400°F.

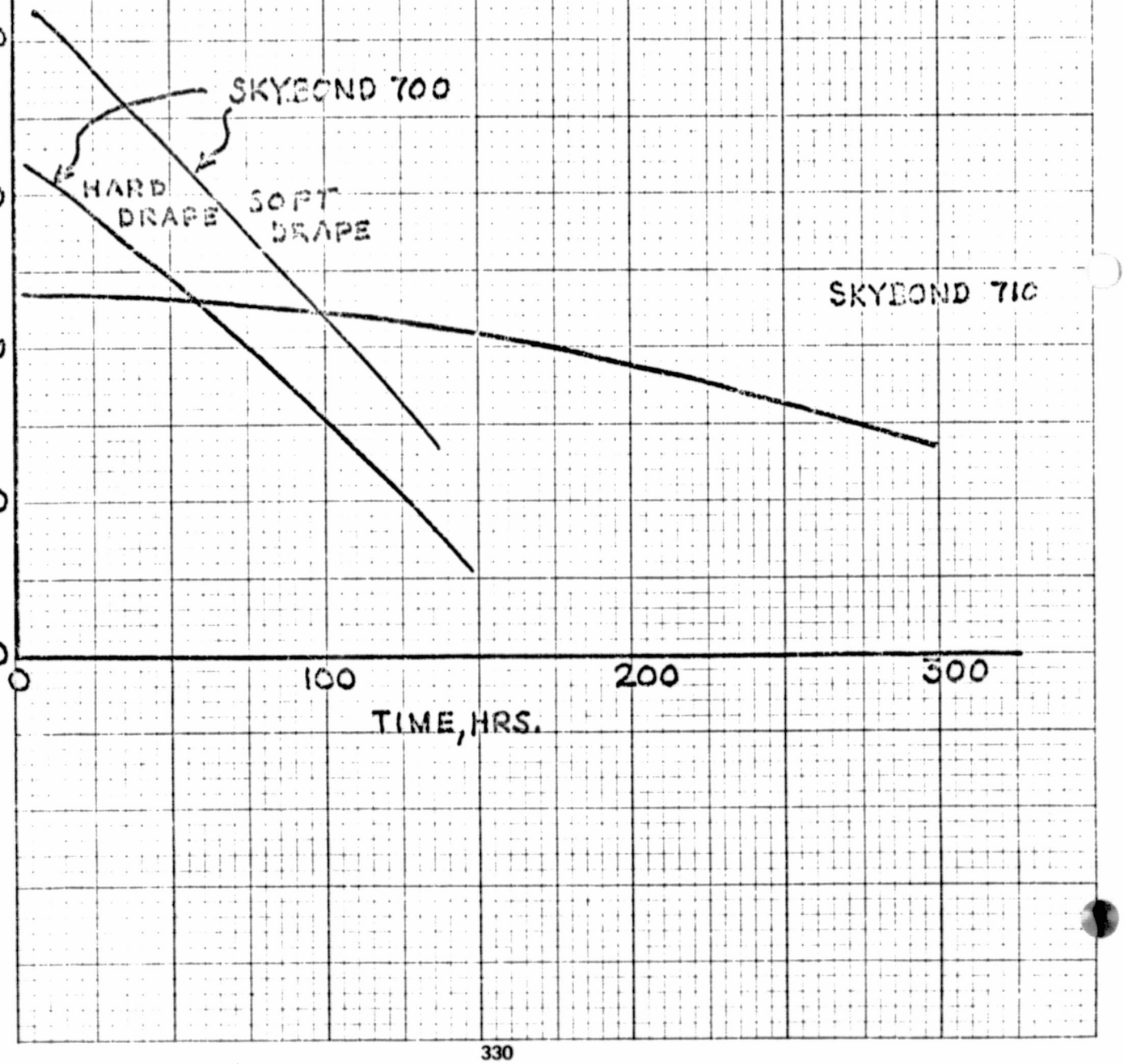
FIG. 6

FLEX AGING

SKYBOND® 700 vs. SKYBOND 710

VACUUM BAG LAMINATES

@ 700°F, AIR



SPAULDING MOSS COMPANY
BOSTON 10, MASS.
MADE IN U.S.A.

NO. 2-10 SEMCO GRAPH PAPER
10 X 10 PER INCH

FIG. 7

SKYBOND® 700 vs EXP. SKYBOND 710

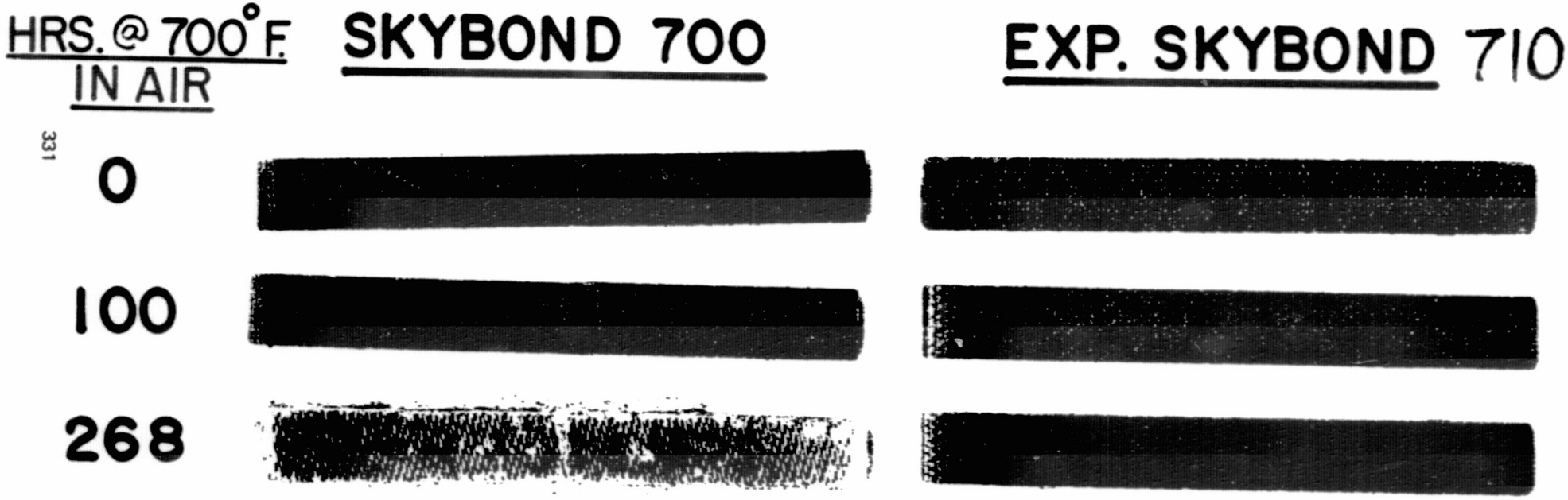
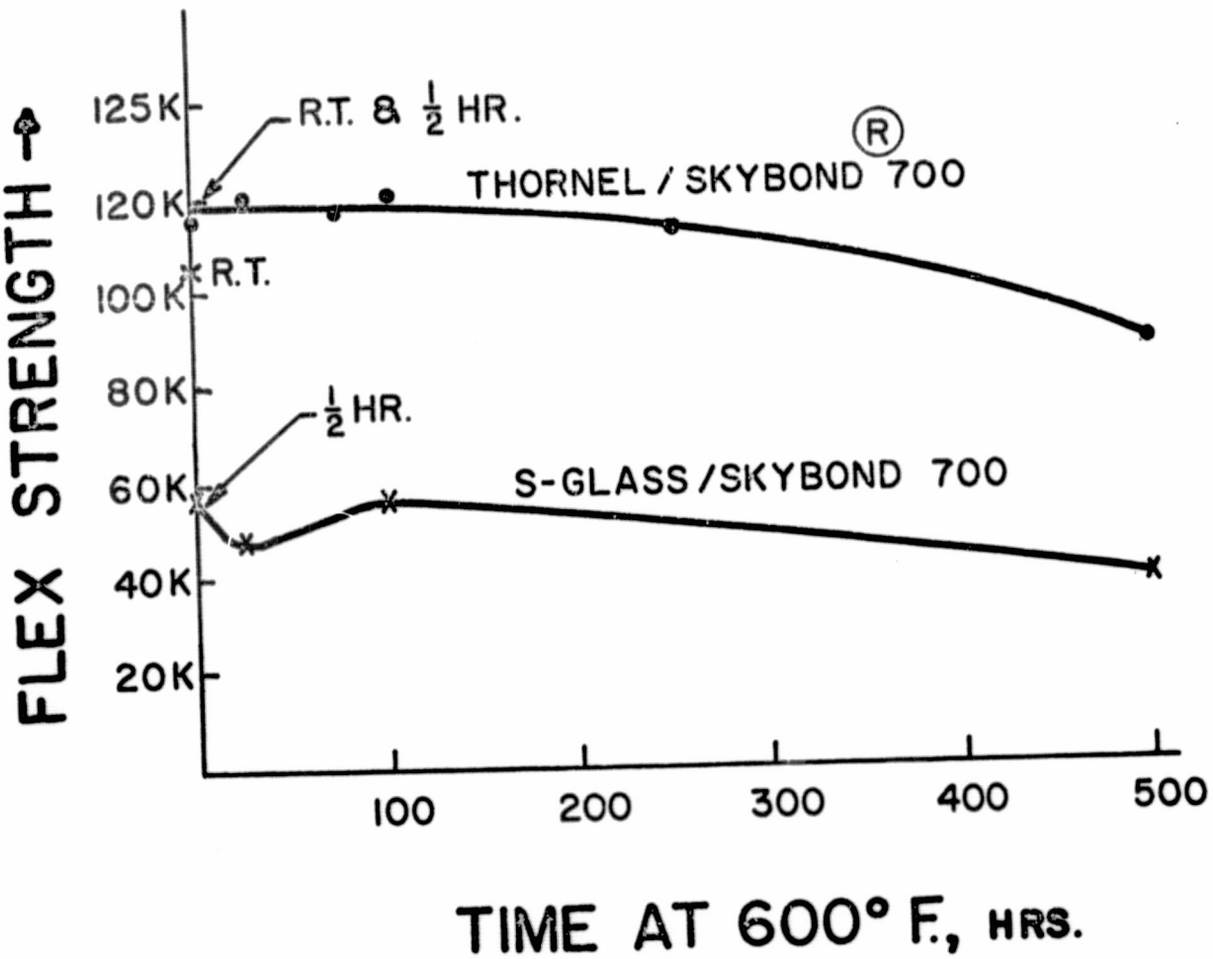


FIGURE 8

EFFECT OF SUBSTRATE SKYBOND® 700 COMPOSITES



-BROWNING & MARSHALL (U.DAYTON, AFML)

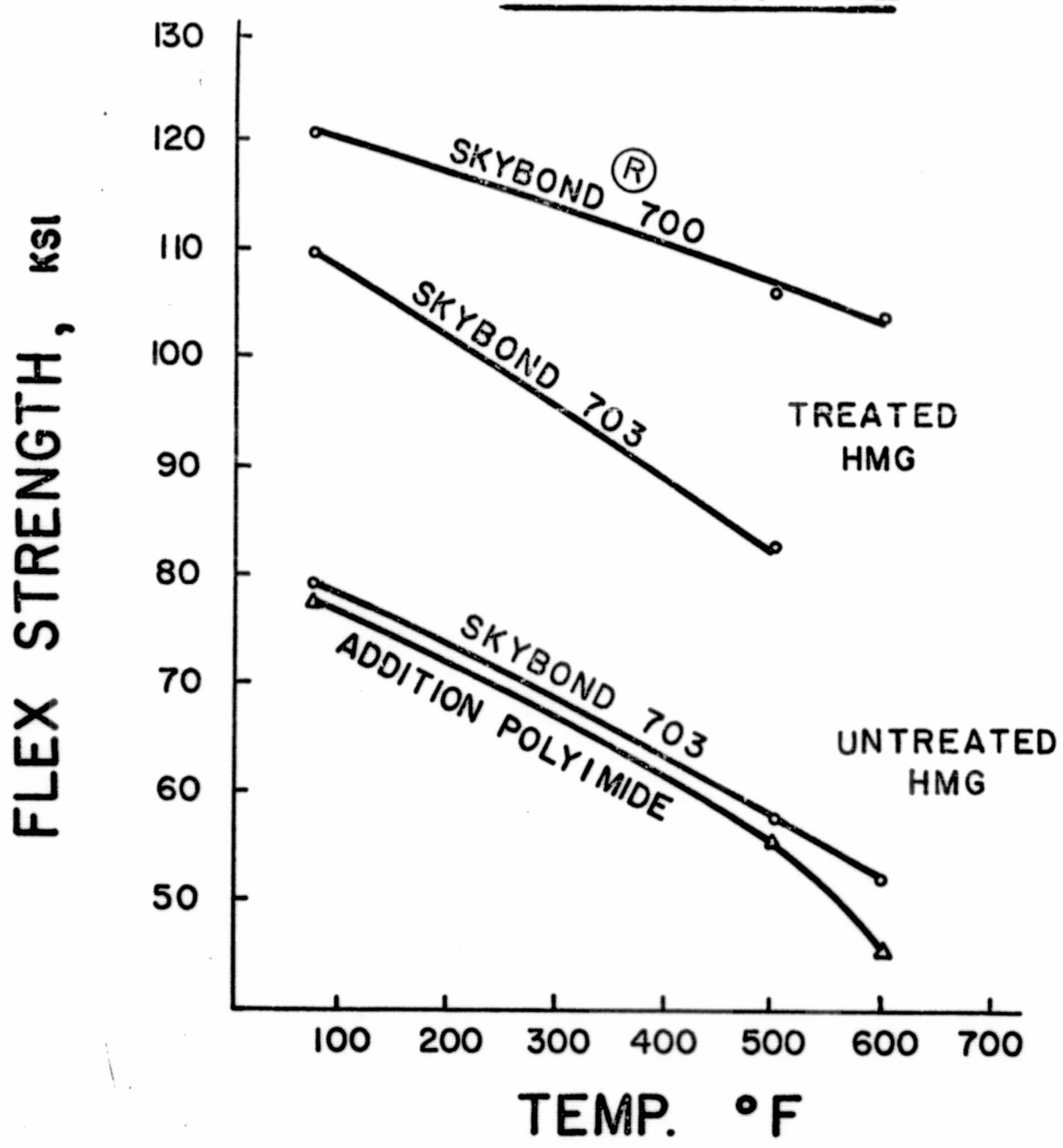
FIGURE 9

GRAPHITE / POLYIMIDE

FLEX STRENGTH

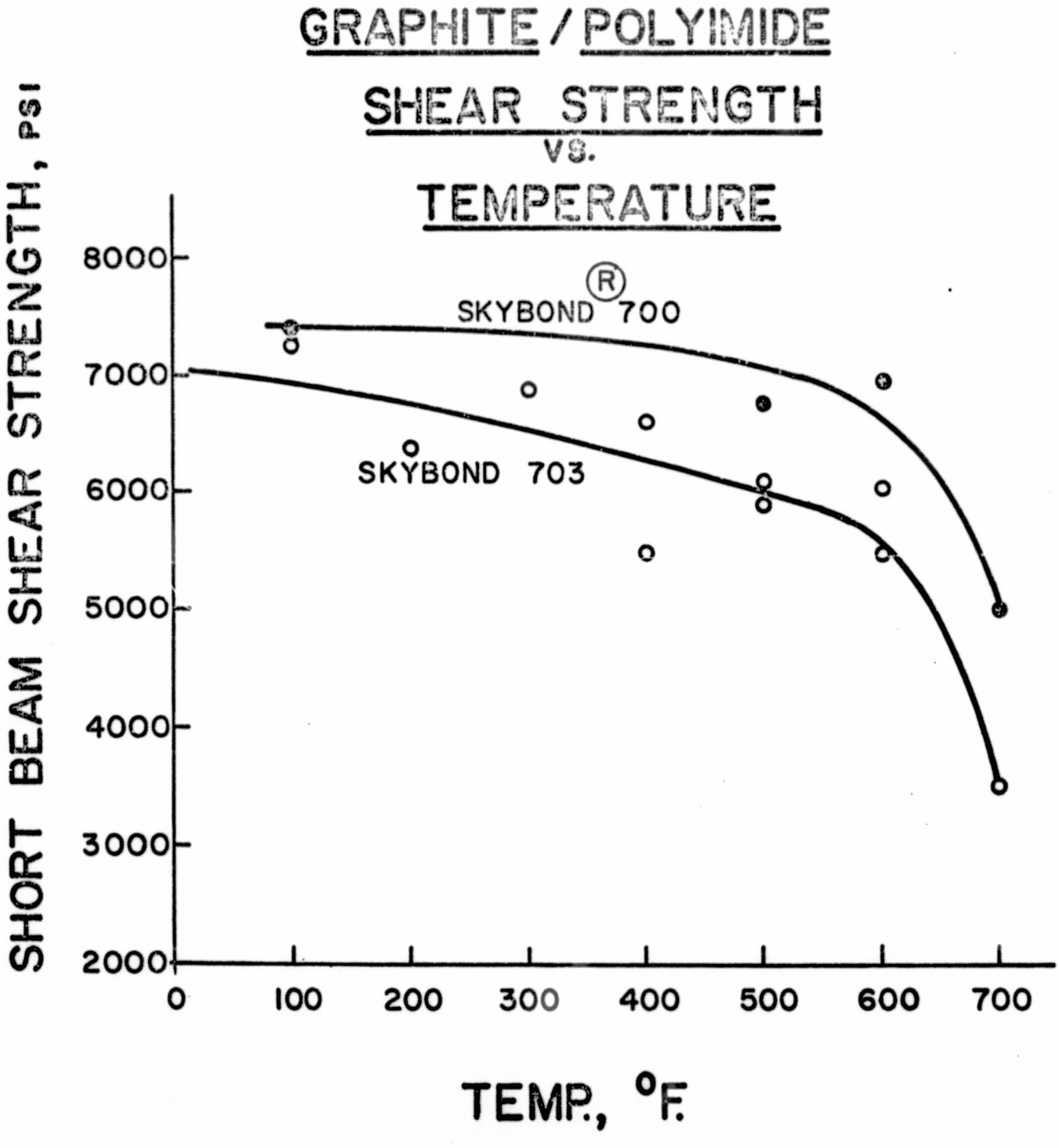
vs.

TEMPERATURE



-PIKE (U.A.C.)

FIGURE 10

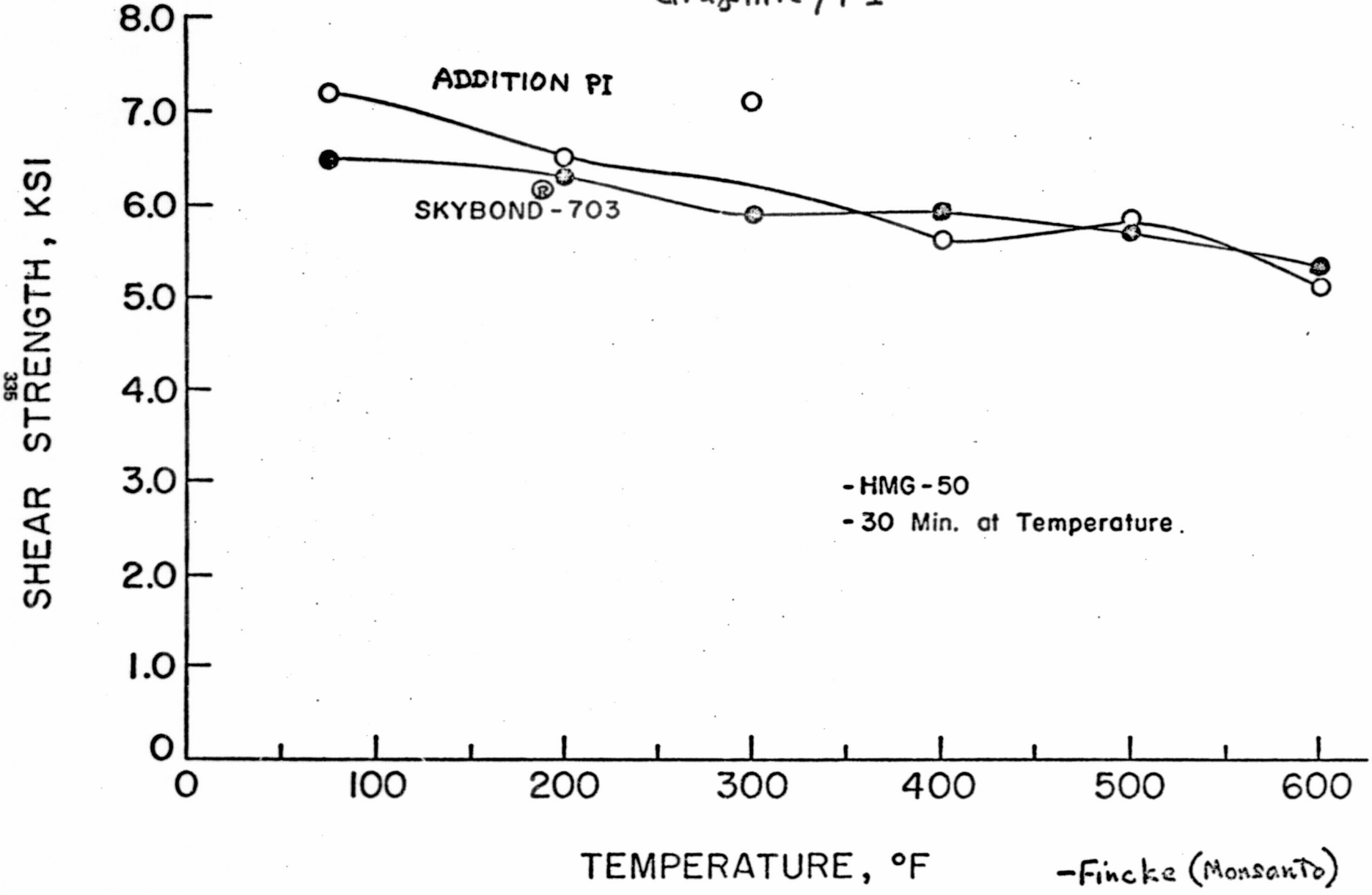


– PIKE (U.A.C.)

FIG. 11

Shear Strength vs Temperature

Graphite / PI



-Fincke (Monsanto)

Shear Strength vs Heat Aging at 600 °F

Graphite / PI

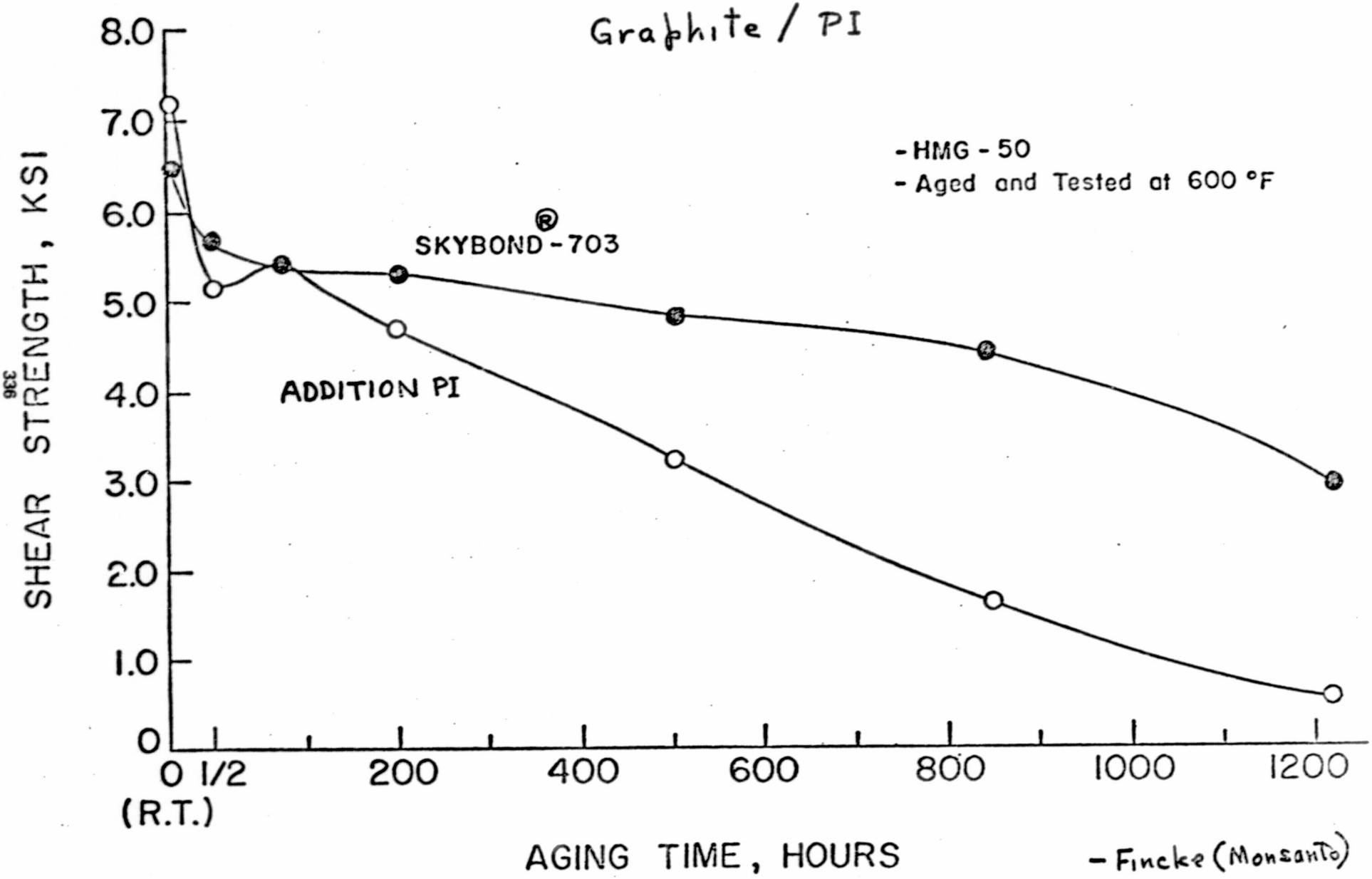
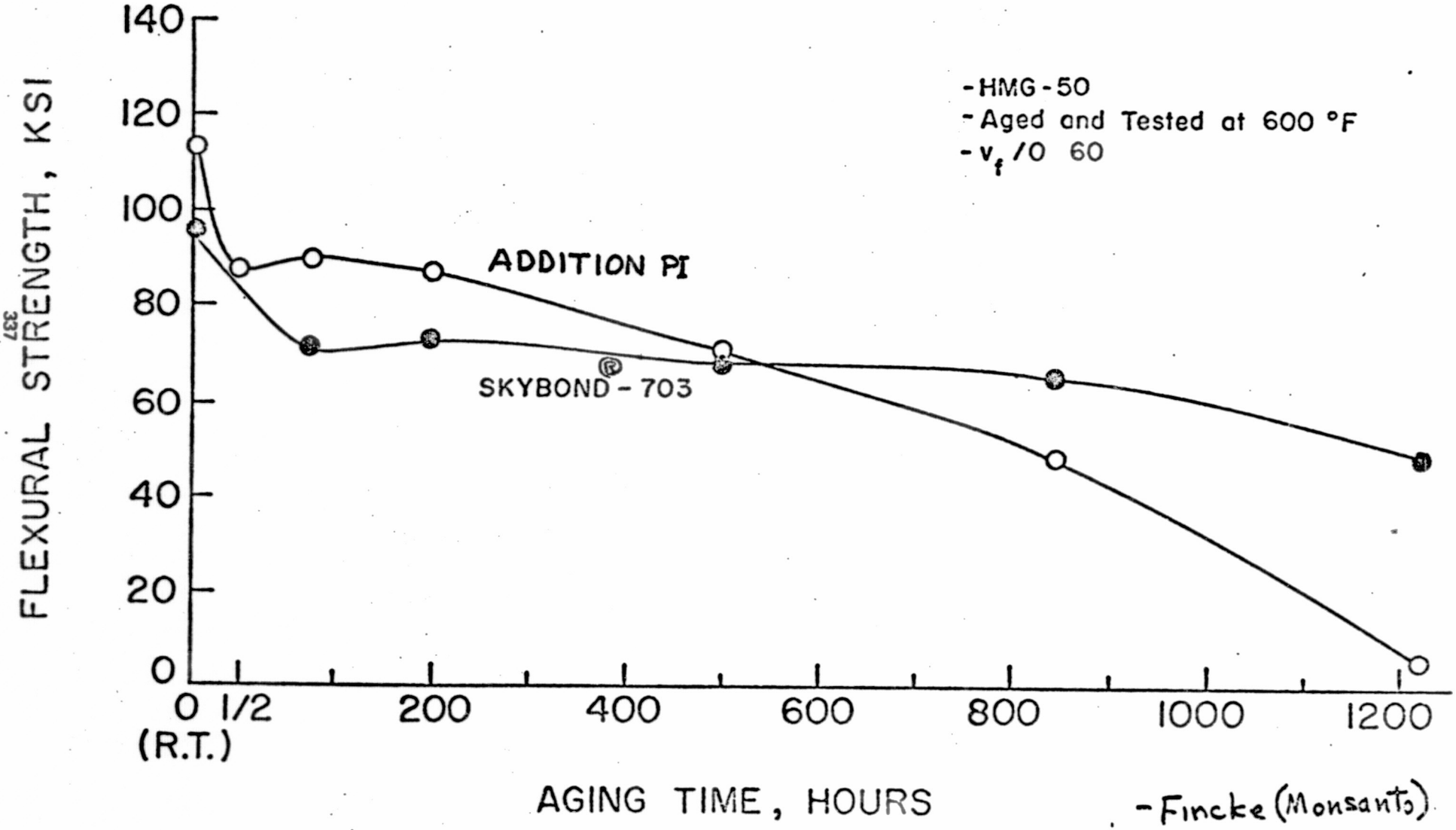


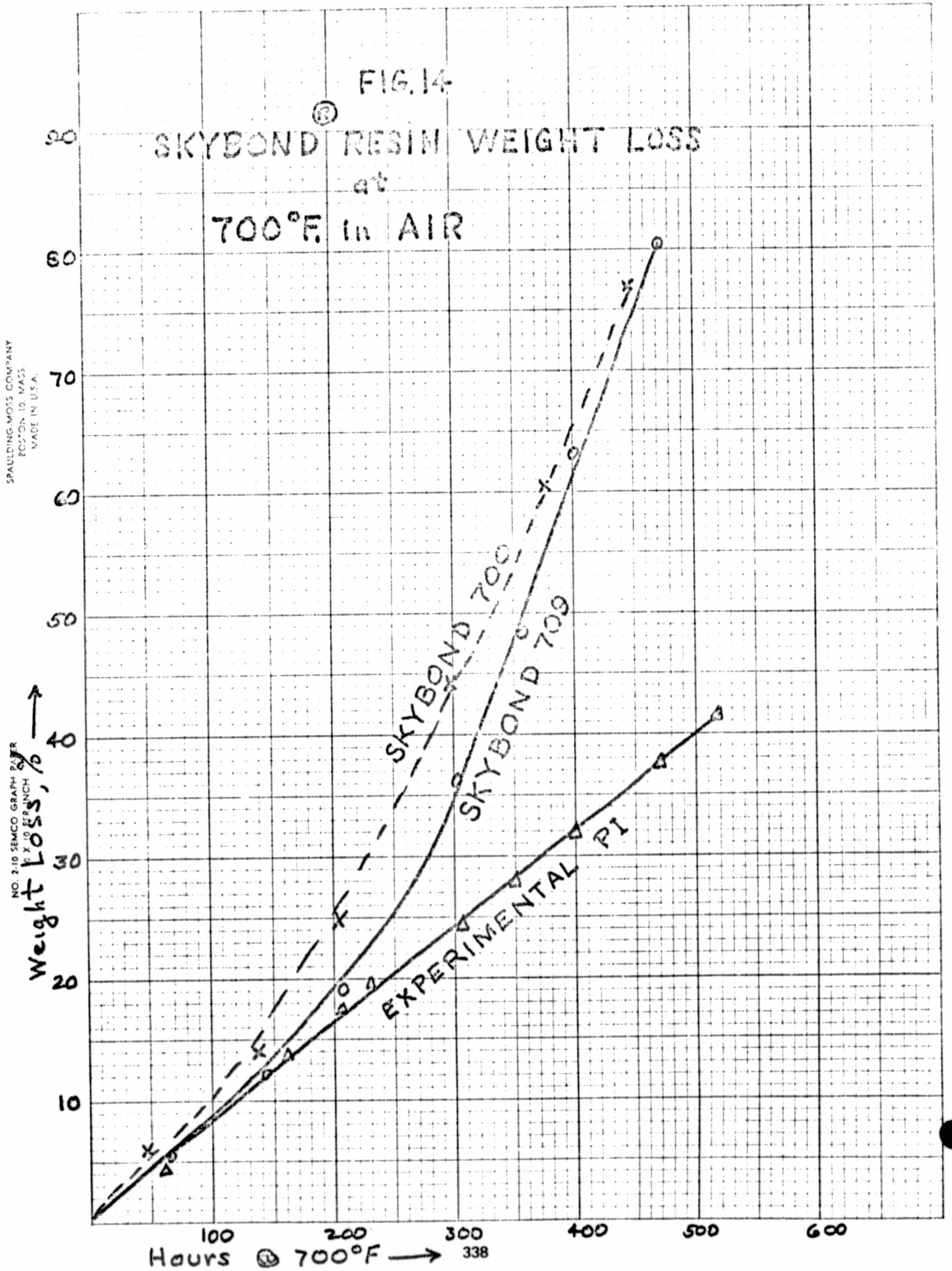
FIG. 13

Flexural Strength vs Heat Aging at 600 °F

Graphite / PI



-Fincke (Monsanto)


FIG. 14
SKYBOND® RESIN WEIGHT LOSS
at
700°F. in AIR
Weight Loss, % →
Hours @ 700°F →
SKYBOND 700
SKYBOND 709
EXPERIMENTAL PI
10
20
30
40
50
60
70
80
100
200
300
400
500
600
SPAULDING-MOSS COMPANY
BOSTON 10, MASS.
MADE IN U.S.A.
NO. 2-10 SEMCO GRAPH PAPER
5 X 10 PER INCH

ROCKWELL INTERNATIONAL PRESENTATION

ROCKWELL INTERNATIONAL PRESENTATION

GRAPHITE-POLYIMIDE COMPOSITES TECHNOLOGY

339

WILLIAMSBURG, VA.

MARCH 17-19, 1975

STAN YOSHINO, MANAGER
ADVANCED MANUFACTURING TECHNOLOGY
SPACE DIVISION
ROCKWELL INTERNATIONAL

DISCUSSION AREAS

- SPACE DIVISION EXPERIENCES WITH POLYIMIDES - GLASS AND ADVANCED COMPOSITES
- FALL-OUT OF PI FAB. EXPERIENCES
- SHUTTLE REVIEW
- PLANNED ACTIVITIES

EXPERIENCES WITH PI - GLASS

- GLASS PI FOR FIRE PROTECTION

  APOLLO - FOOD BOX, SLUFF GUARDS, CIRCUIT BREAKER HOUSING, SHAVER HOUSING, BATTERY SHELVES, ELECTRICAL CONNECTORS

  SKYLAB - URINE CHILLER, FOOD TRAY, CASSETTE HOUSING, WASTE CONTAINERS

  SHUTTLE (PROPOSED) - ALL OF THE ABOVE PLUS SLIDING PANELS, WALL PANELING, ADJUSTABLE SHUTTERS, AIR CONDITIONING DUCTS, LOW-COST PI CORE PANELS

  COMMERCIAL - FIREMAN HELMETS, ACOUSTIC PANELS, AIR VANE HOUSING AIRCRAFT INTERIOR PANELS

- WORK RESTRICTED TO CONDENSATION TYPE PI PREPREG VACUUM BAG AUTOCLAVE CURE

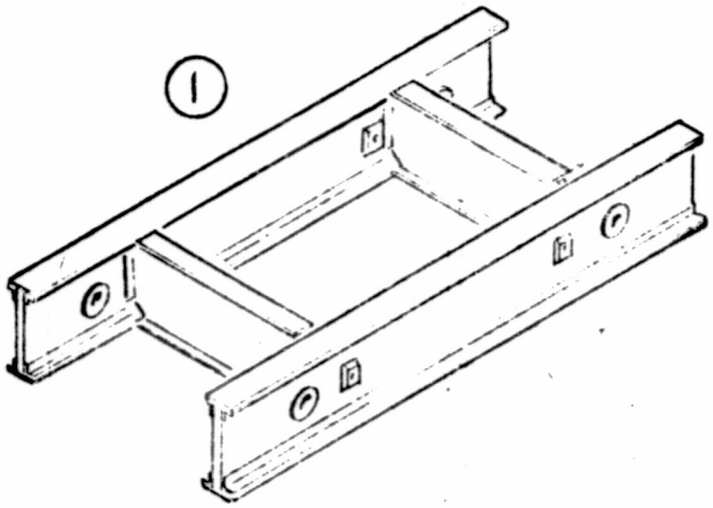
- EVEN WITH LOW RESIN CONTENT/HIGH VOID, PI GLASS PV COUPONS AS STRONG AS EPOXIES

- SHUTTLE 23% O_2 77% N_2 - FAA TYPE MATERIALS WILL QUALIFY

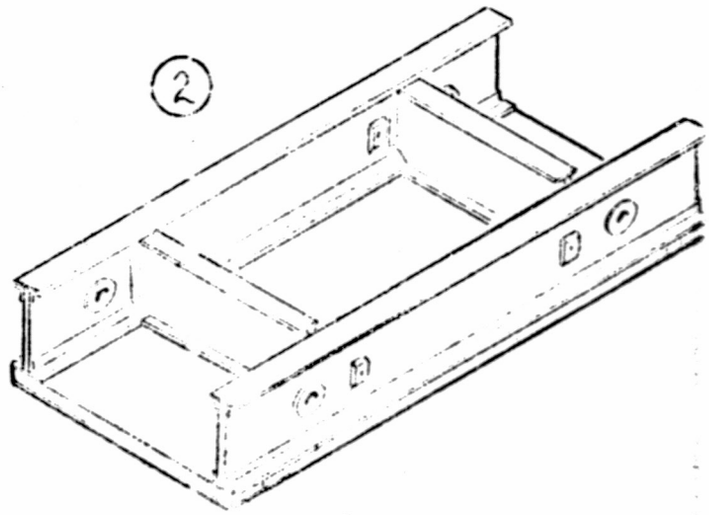
EXPERIENCE WITH PI/ADVANCED COMPOSITES

- BORON/PI (COND. TYPE) WING BOX BEAM FABRICATED AT CAD
  - ENCOUNTERED NUMEROUS PROBLEMS - FAILED PROOF TEST
- GRAPHITE/PI (ADD TYPE) WING BOX BEAM FABRICATED AT SPACE DIVISION
  - DEMONSTRATED SUCCESSFUL FAB. PROCEDURES - DESIGN FAILURE AT 80% DESIGN LIMIT
- FIVE 4-1/2' X 11' GRAPHITE PI (KERIMID 601 MOD II) SKINS FOR AFT BODY FLAP COMPLETED
- FOUR STABILITY RIB SKINS 4-1/2' LONG 4' - 1.[illegible]" IN WIDTH GRAPHITE PI (HX 580 MOD II) COMPLETED
- TEST PANELS T-300 5-MIL WOVEN FABRIC W/MONSANTO 703 FABRICATED
- PI - GRAPHITE SKIN H/C SANDWICH PANELS W/NR-150 ADHESIVE FABRICATED AND IN TEST

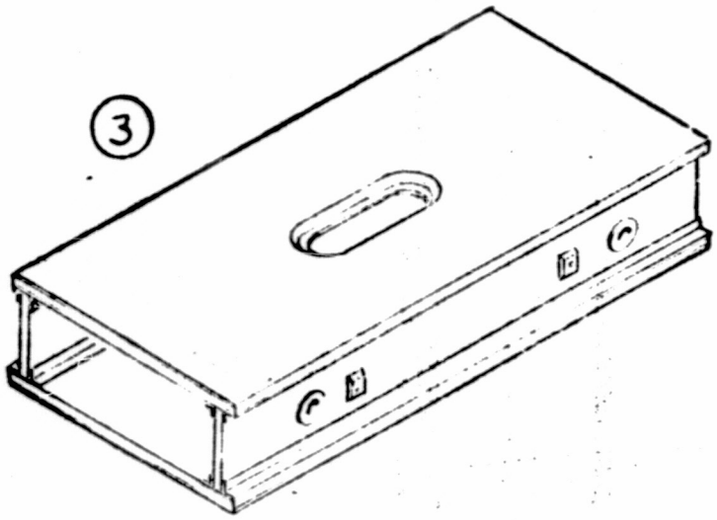
POLYIMIDE BOX BEAM ASSY



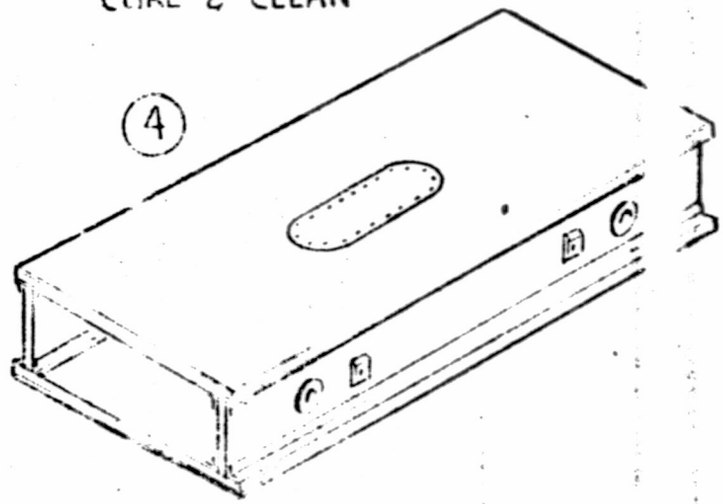
SUB ASSY "A"
PREFIT & BOND SPAR & RIBS CURE & CLEAN



SUB ASSY "B" PREFIT & BOND SUB ASSY "A" TO LWR PANEL CURE & CLEAN



MAIN ASSY
PREFIT & BOND SUB ASSY "B" TO UPPER PANEL

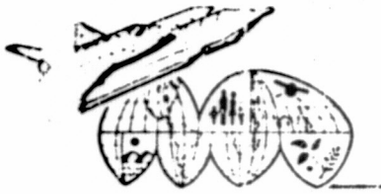


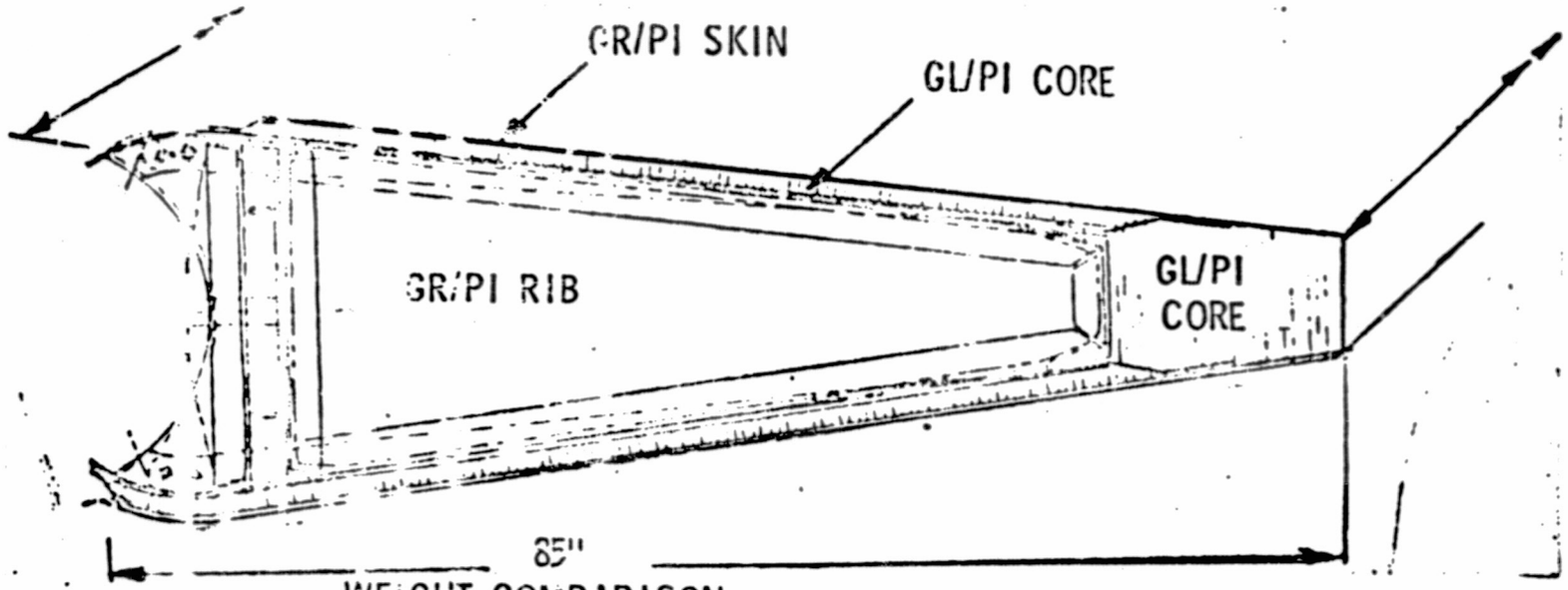
LAY-OUT & LOCATION IN DOOR, PLACE DOOR IN POSITION, DRILL THRU DOOR & UPPER PANEL, ADD NUTS & ADD DOOR

(5) INSPECT

(6) PACKAGE & SHIP

COMPOSITE BODY FLAP





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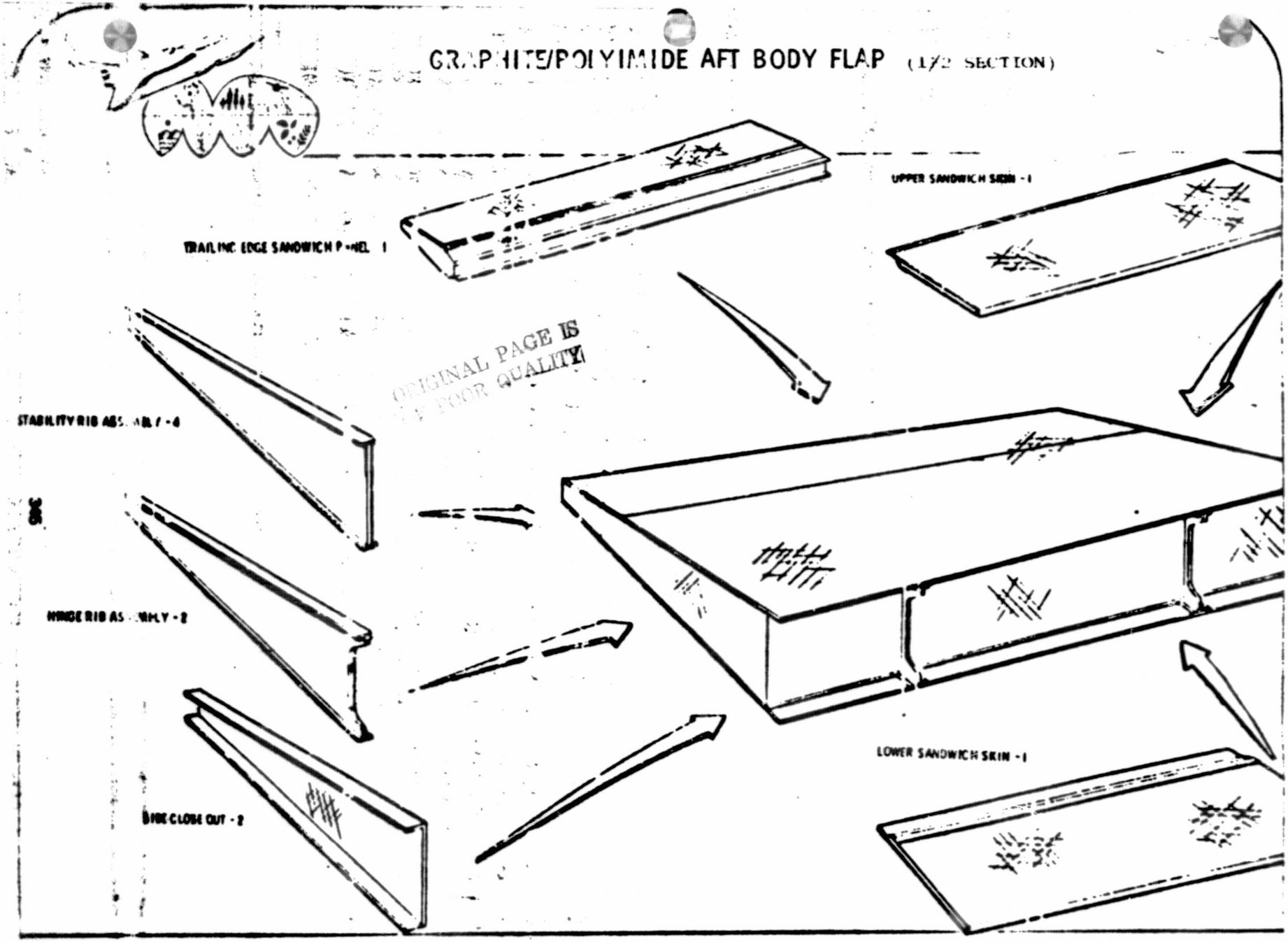
WEIGHT COMPARISON

ITEM	BASELINE	GRAPHITE / PI 500°F
STRUCTURE	502	367
TPS	755	630
TOTAL WT.	1257	997
		-260

260 POUND WT. SAVING

INSTALLATION AFT BODY FLAP: SHUTTLE 101 - MARCH '76, SHUTTLE 102 - JUNE '77

GRAPHITE/POLYIMIDE AFT BODY FLAP (1/2 SECTION)



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Space Division
North American Rockwell

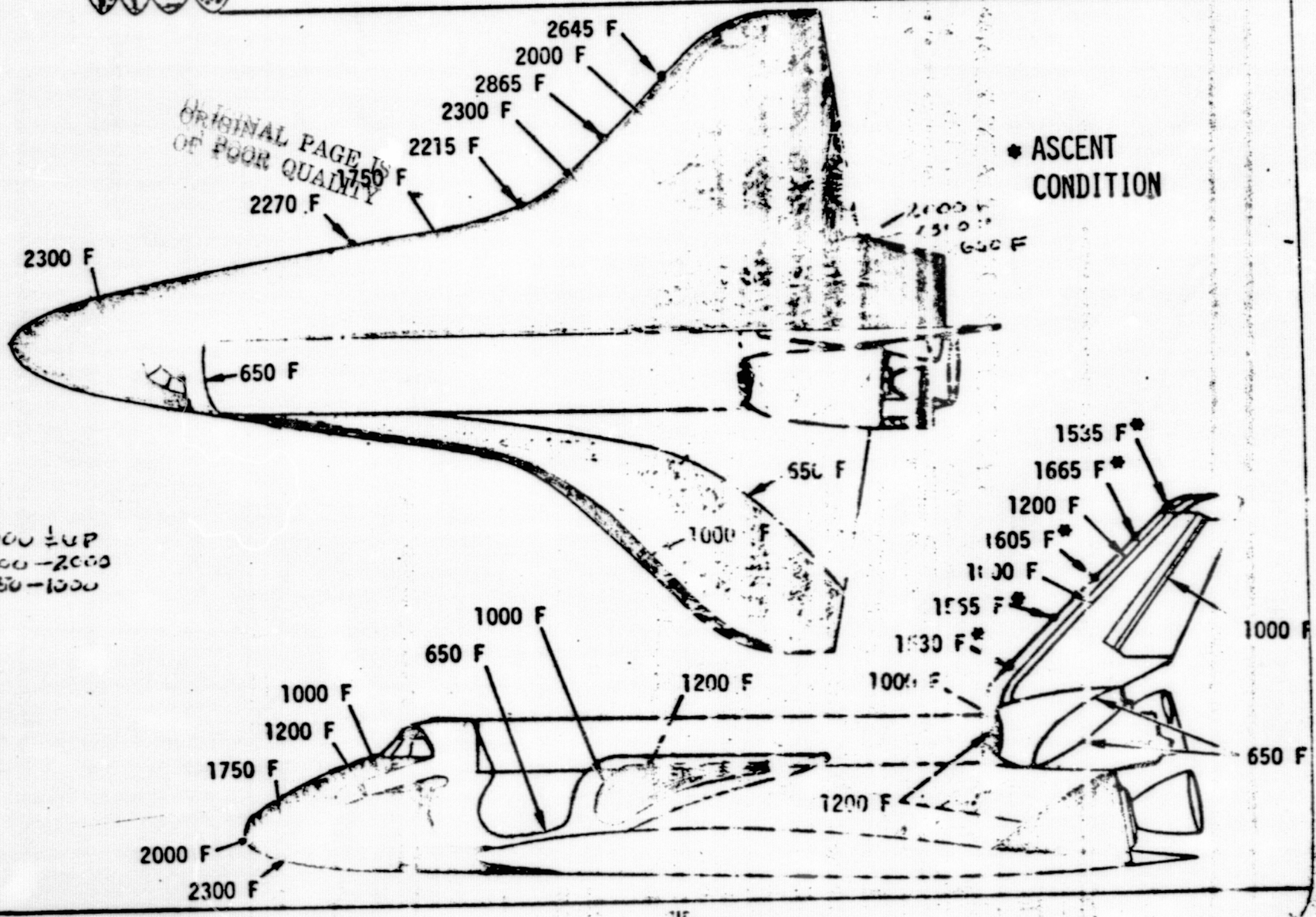
SHUTTLE REVIEW

- SHUTTLE ISOTHERM & STRUCTURES
- BASELINE ADVANCED COMPOSITE STRUCTURES FOR SHUTTLE
- POSSIBLE APPLICATION OF ADVANCED COMPOSITES

ORBITER ISOTHERMS



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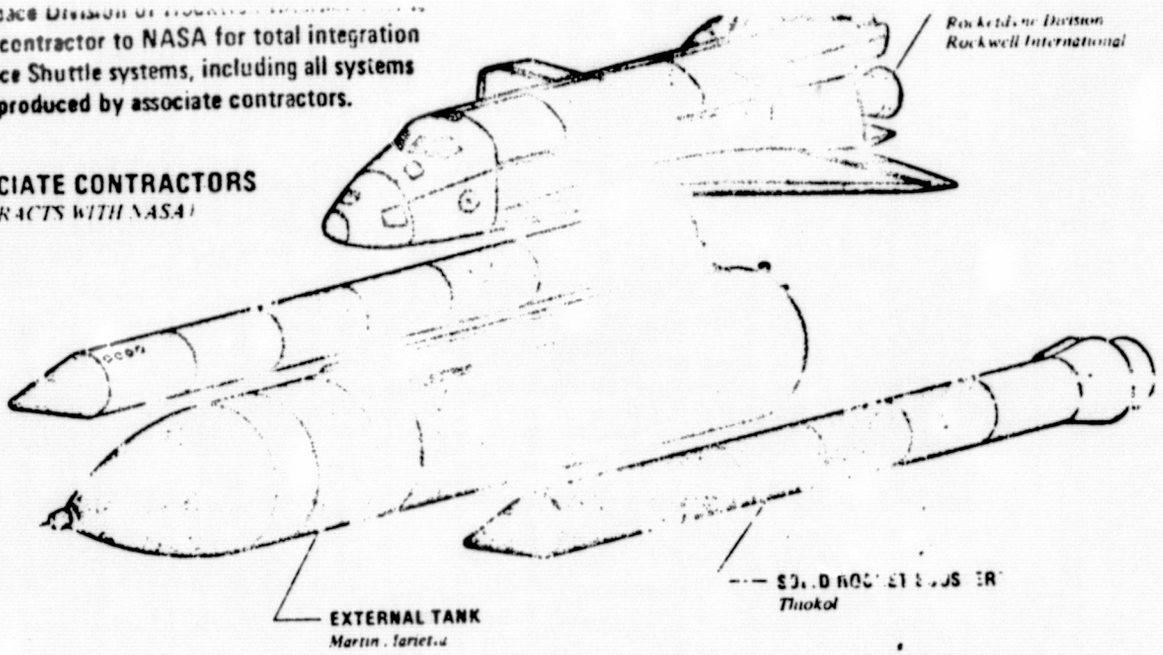
North American
Aerospace Operations

Space Division
Rockwell International

SPACE SHUTTLE CONTRACTORS

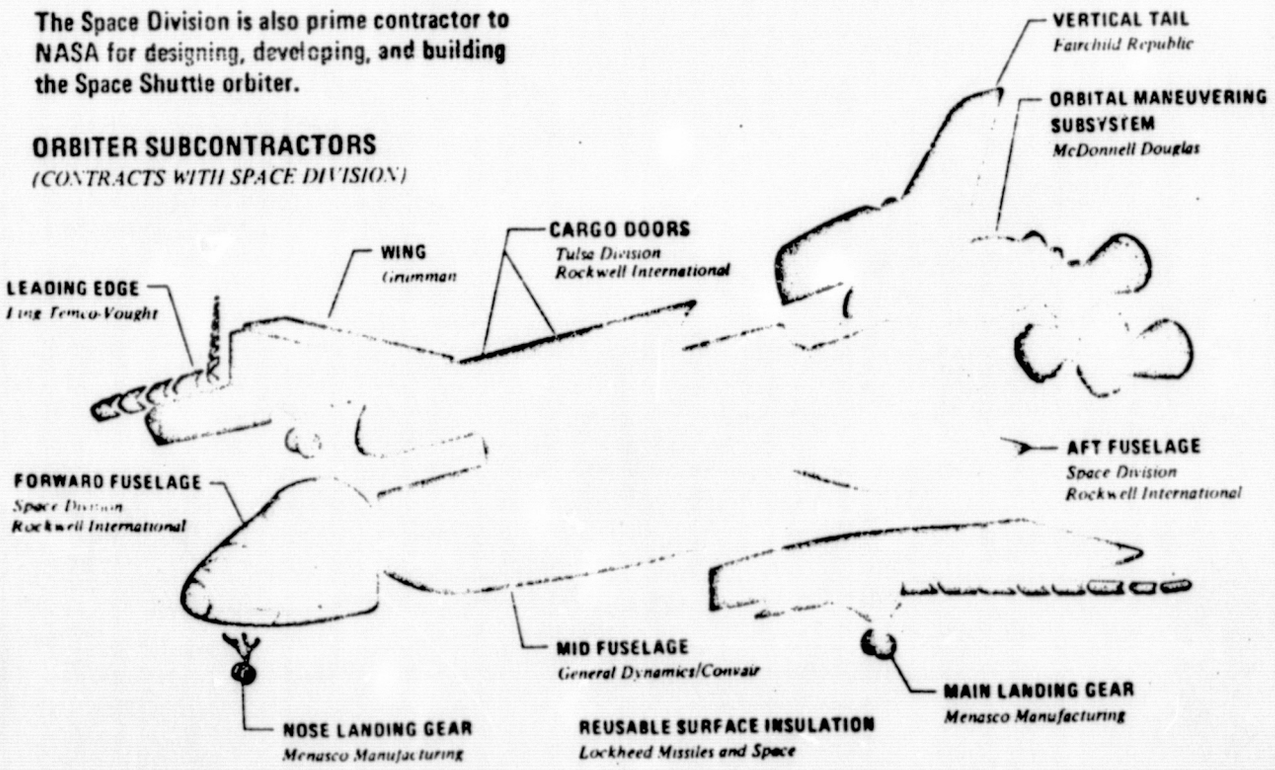
The Space Division of Rockwell International is prime contractor to NASA for total integration of Space Shuttle systems, including all systems being produced by associate contractors.

ASSOCIATE CONTRACTORS
(CONTRACTS WITH NASA)



The Space Division is also prime contractor to NASA for designing, developing, and building the Space Shuttle orbiter.

ORBITER SUBCONTRACTORS
(CONTRACTS WITH SPACE DIVISION)



These illustrations do not indicate all Space Shuttle subcontractors selected, nor have all Space Shuttle subcontracts been awarded.

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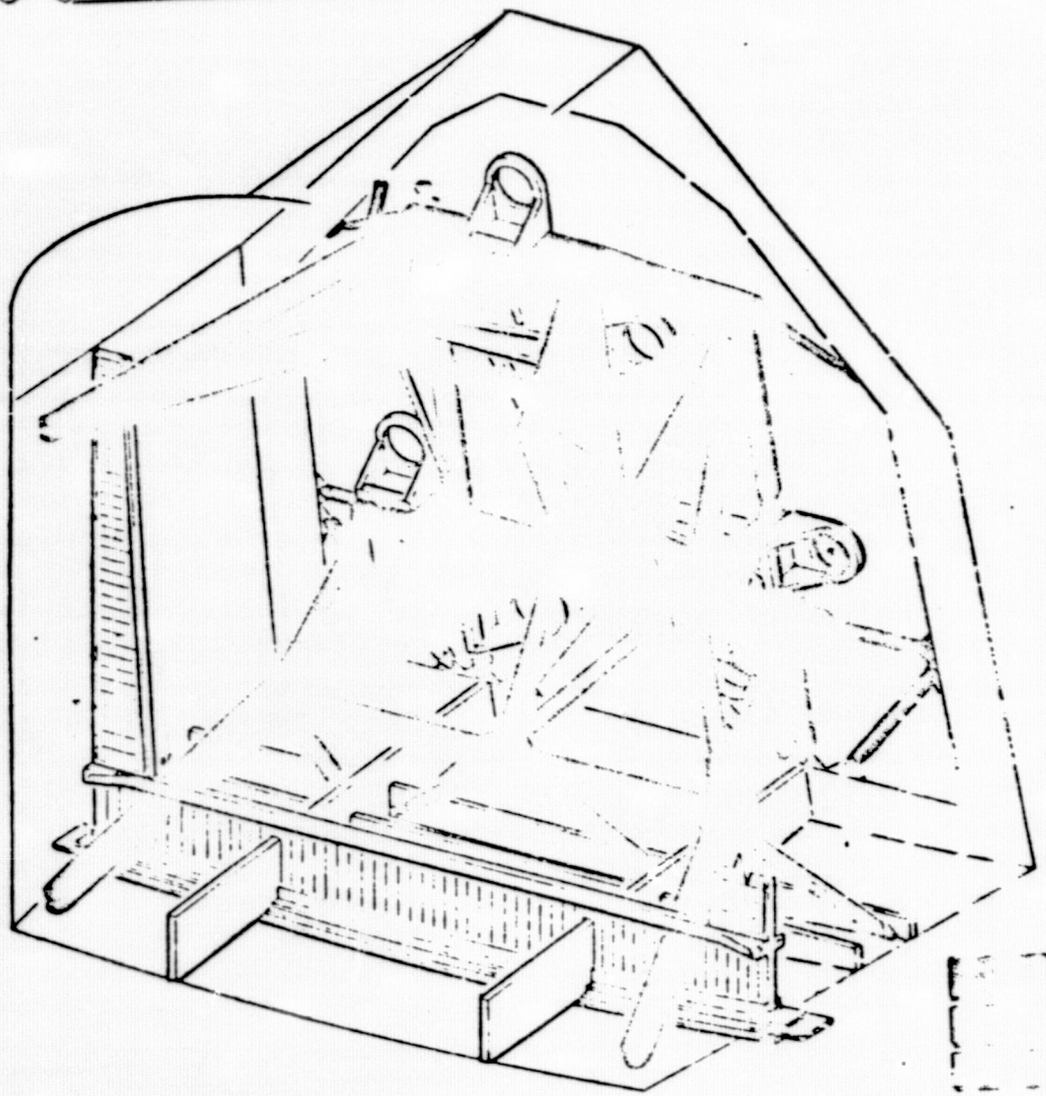
BASELINE ADVANCED COMPOSITE STRUCTURES

	MATERIAL	WEIGHT SAVINGS (LBS)
AFT THRUST STRUCTURE	BORON/EPOXY	900
CARGO BAY DOORS	GRAPHITE/EPOXY	1070
MID FUSELAGE TRUSS TUBES	BORON/ALUMINUM	180
*OMS POD	GRAPHITE/EPOXY	300
**AVIONICS BAY SHELVES	BORON/ALUMINUM	350
*PURGE & VENT LINES	KEVLAR/EPOXY	200

*IN DESIGN

**DEMONSTRATION TEST COMPLETED

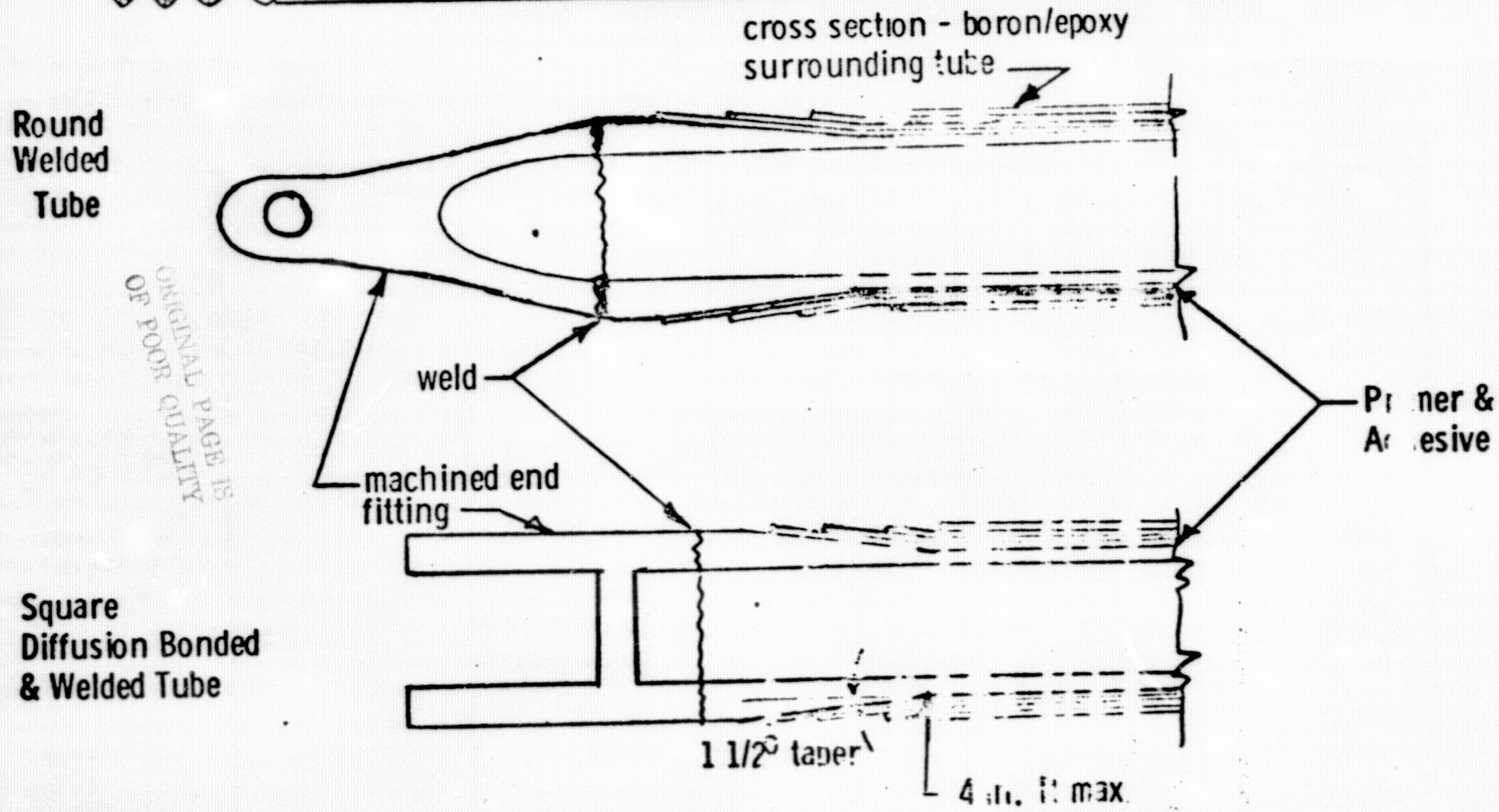
AFT FUSELAGE THRUST STRUCTURE



Ti DIFFUSION BONDED
Ti ROUND - TUBE WELDI
Ti M.CHINED

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BORON/EPOXY TITANIUM TRANSITION DESIGNS



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PAYLOAD BAY DOOR DESIGN CONCEPT WEIGHT COMPARISON

ITEM	BASELINE AL/HC (350°F)	COMPOSITE GR/EP (350°F)	COMPOSITE GRAPHITE POLYIMIDE WITH MAX TEMP OF 500°F	550°F	600°F
STRUCTURAL SYSTEM (LBS)	4150	3050	3050	3050	3050
STRUCT. WT. OVER BASELINE (LBS)	0	-1100	-1100	-1100	-1100
TPS WT.* DUE TO COMPL. REMOVAL (LBS)	0	0	0	-151	-151*
TPS WT. DUE TO THICKNESS CHANGE (LBS)	0	30	-43	-64	-80
TOTAL TPS WT. (LBS)	0	30	-38	-215	-231
TCS WT. (LBS)	0	0	32	140	150
TOTAL WT. OVER BASELINE (LBS)	0	1070	-1105	1175	1181

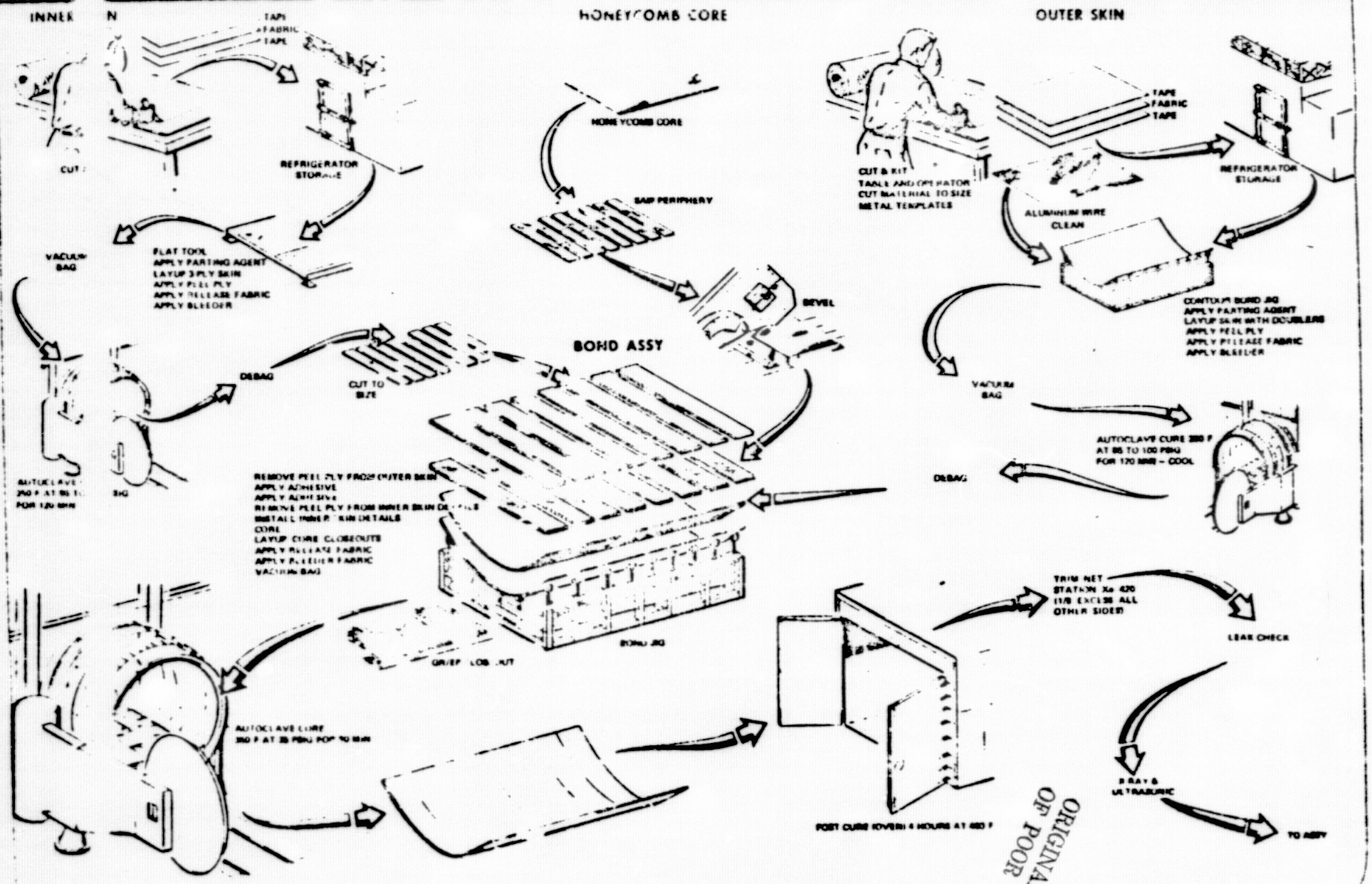
* BASED ON ENTRY TRAJECTORY TN 14040

** DUE TO PRESENT BONDLINE TEMP. LIMIT OF 550°F

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15 FT PAYLOAD BAY DOOR GRAPHITE EPOXY

BONDED PANEL

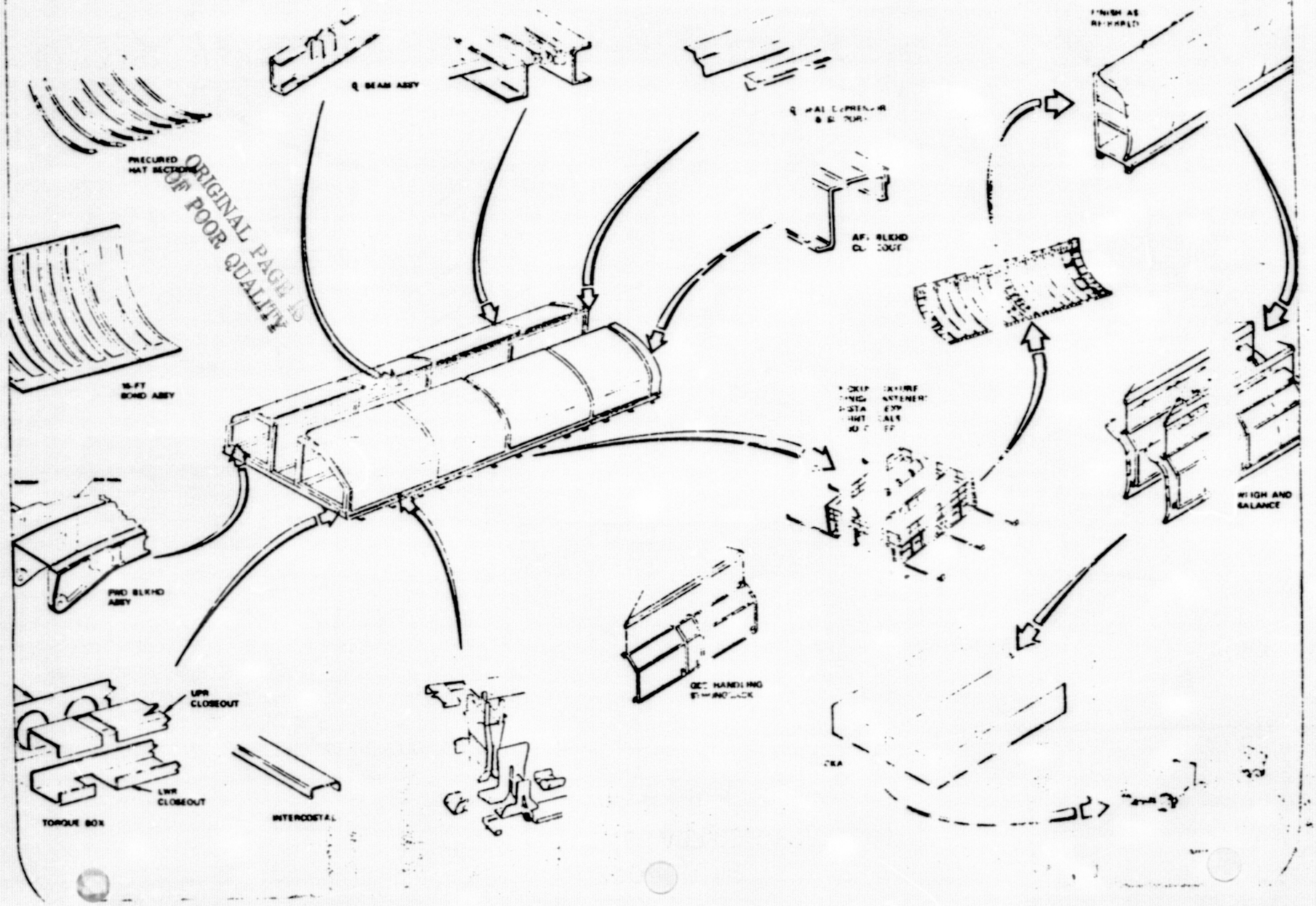


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PAYLOAD BAY DOORS - GRAPHITE/EPOXY

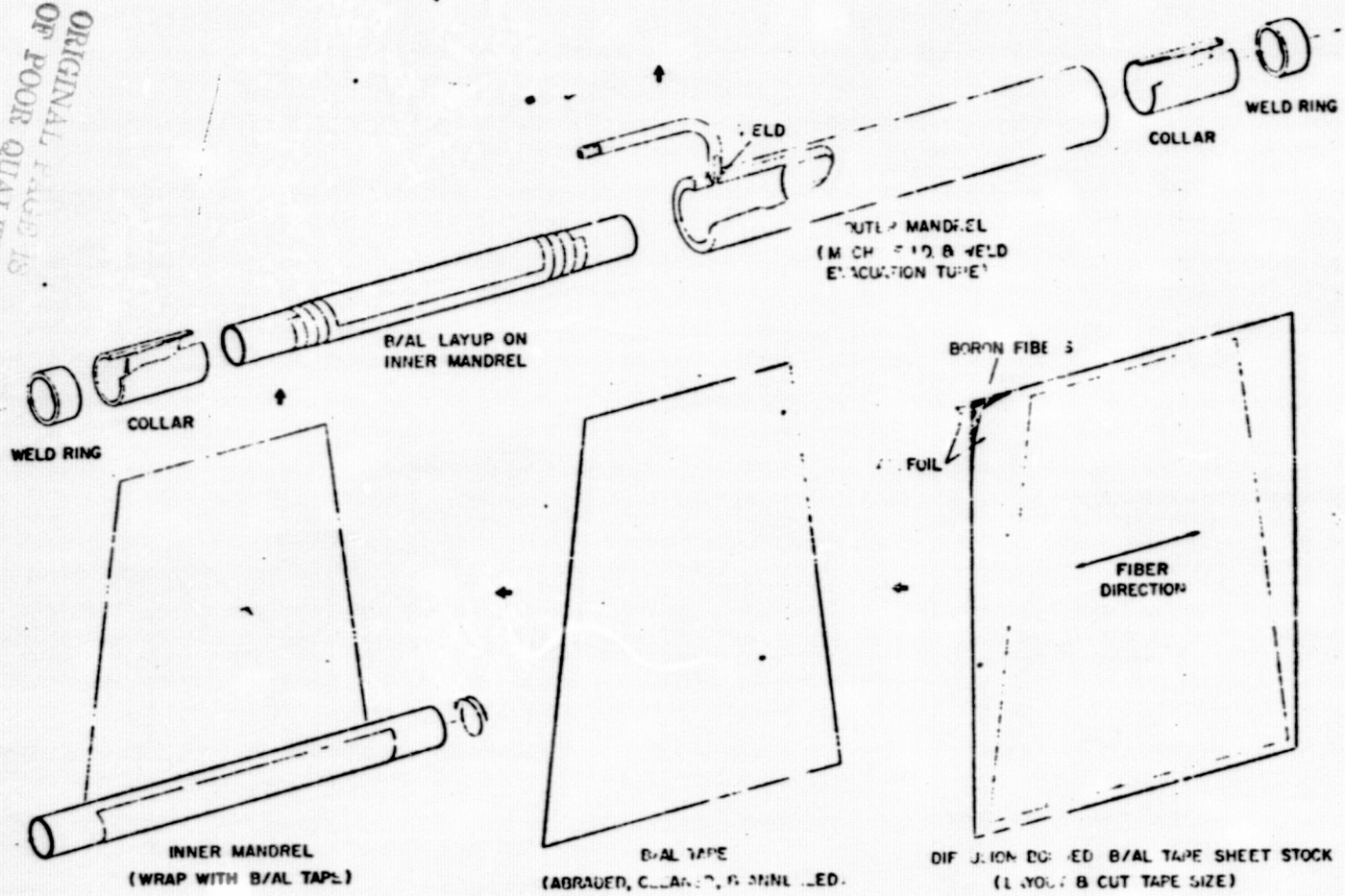
MANUFACTURING FLOW



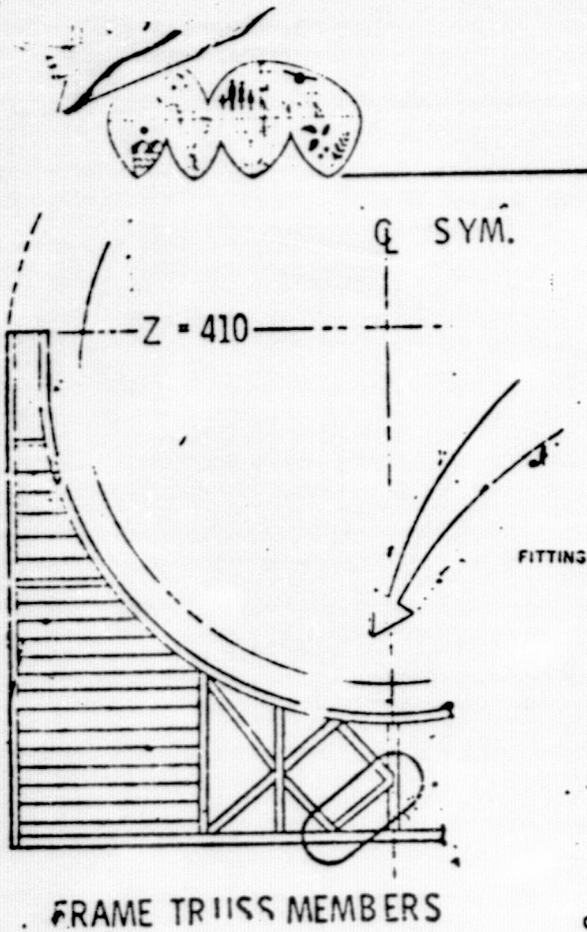
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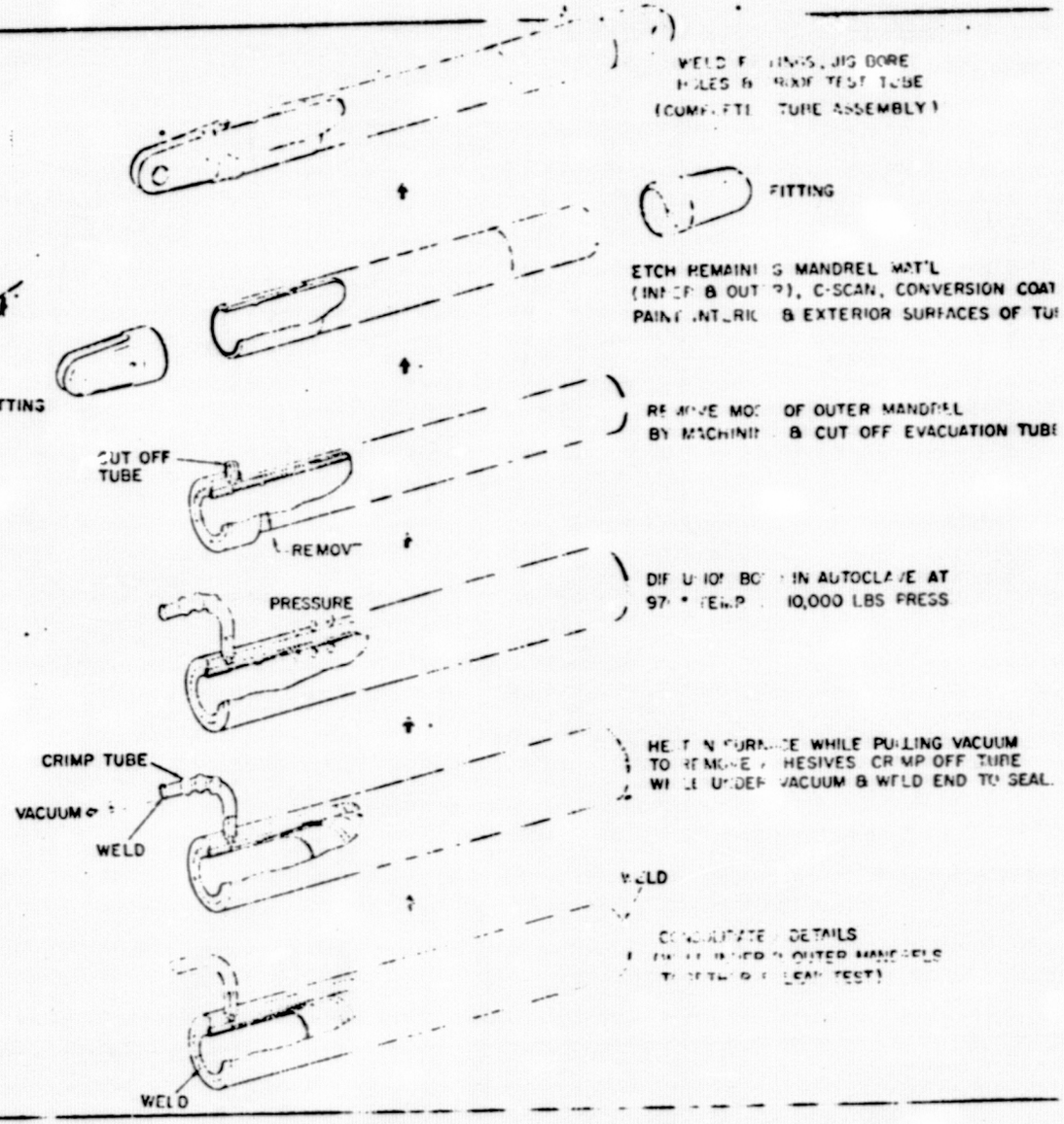
BORO ALUMINUM TUBE FABRICATION

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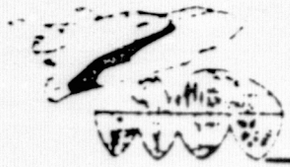
BORON / ALUMINUM TUBE FABRICATION

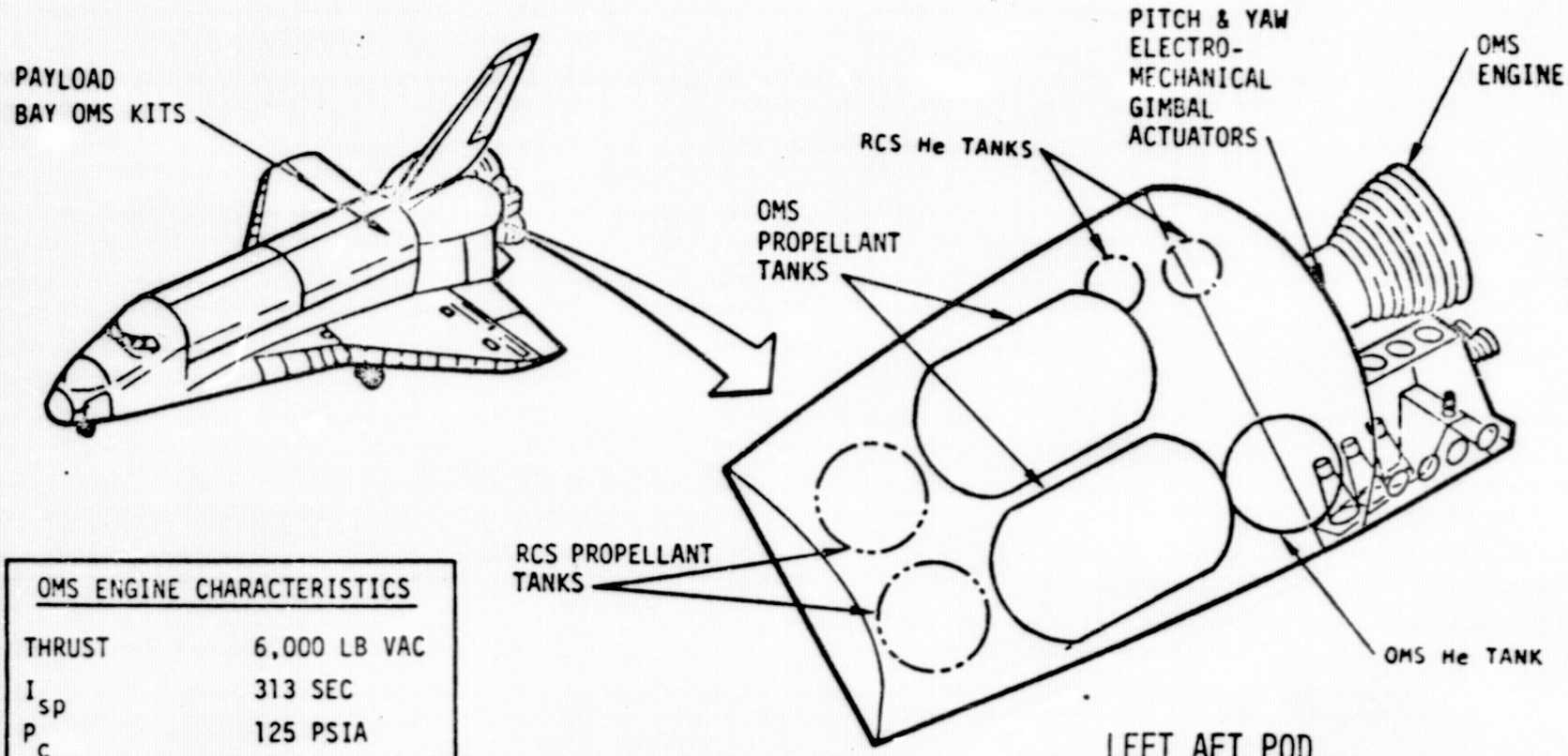




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ORBITAL MANEUVER SUBSYSTEM





LEFT AFT POD

OMS ENGINE CHARACTERISTICS	
THRUST	6,000 LB VAC
I_{sp}	313 SEC
P_c	125 PSIA
MIXTURE RATIO	1.65:1
GIMBAL CAPABILITY	±4 DEG, PITCH ±8 DEG, YAW

OMS TANKAGE CAPACITY	1,000 FT/SEC ΔV	
FUEL WEIGHT - MMH	9,046 LB	USABLE
OXIDIZER WEIGHT - N_2O_4	15,104 LB	USABLE

FALL-OUT OF PI FAB. EXPERIENCES

- o TOOLING

  ALUMINUM: EXCELLENT FOR GLASS FABRIC PI (EXPANSION FACTOR ANALYZED)
  NO SHRINKAGE ALLOWANCE FOR GRAPHITE/PI FLAT SKINS
  PARTS WITH METAL END CLOSEOUTS MUST REMAIN FREE OF TOOL

  PLASTER: COATED WITH RTV FOR ONE PART FAB. ACCOMPLISHED

  STEEL: PREFERRED OVER ALUMINUM BUT HIGHER IN COST IF PART IS NOT FLAT

  KEVLAR/EPOXY: UNDER DEVELOPMENT - DATA TO DATE INDICATE RELATED CHANGES IN DIMENSIONS

  GLASS EPOXY: SIMILAR TO STEEL IN DESIGN

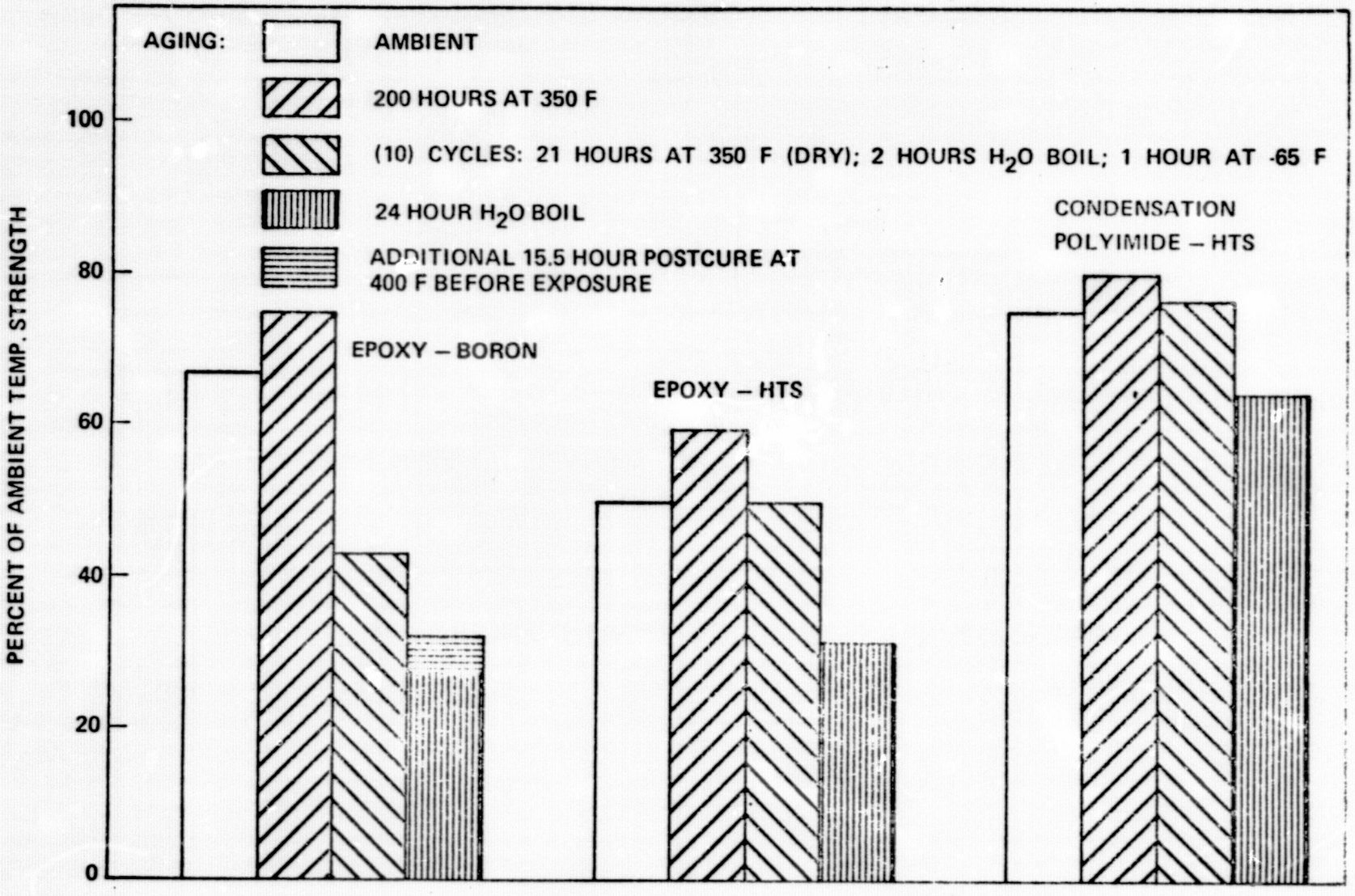
  GRAPHITE EPOXY: UNDER DEVELOPMENT

  GLASSROCK (CERAMIC): REQUIRES INTERNAL HEATING

- o PROCESSING POST CURE - MOST PI PARTS CAN BE POST FORMED DURING
  - IRONING (TEFLON COATED) W/ARMALON SHEET LAY WAY OF NESTING PI PREPREG DRY TAPE
  - SOLVENT REMOVAL DURING CURE MOST IMPORTANT CONTROL
  - PRESENCE OF MOISTURE DURING LAYUP IMPROVES LAMINATE QUALITY

FALL-OUT OF PI FAB. EXPERIENCES

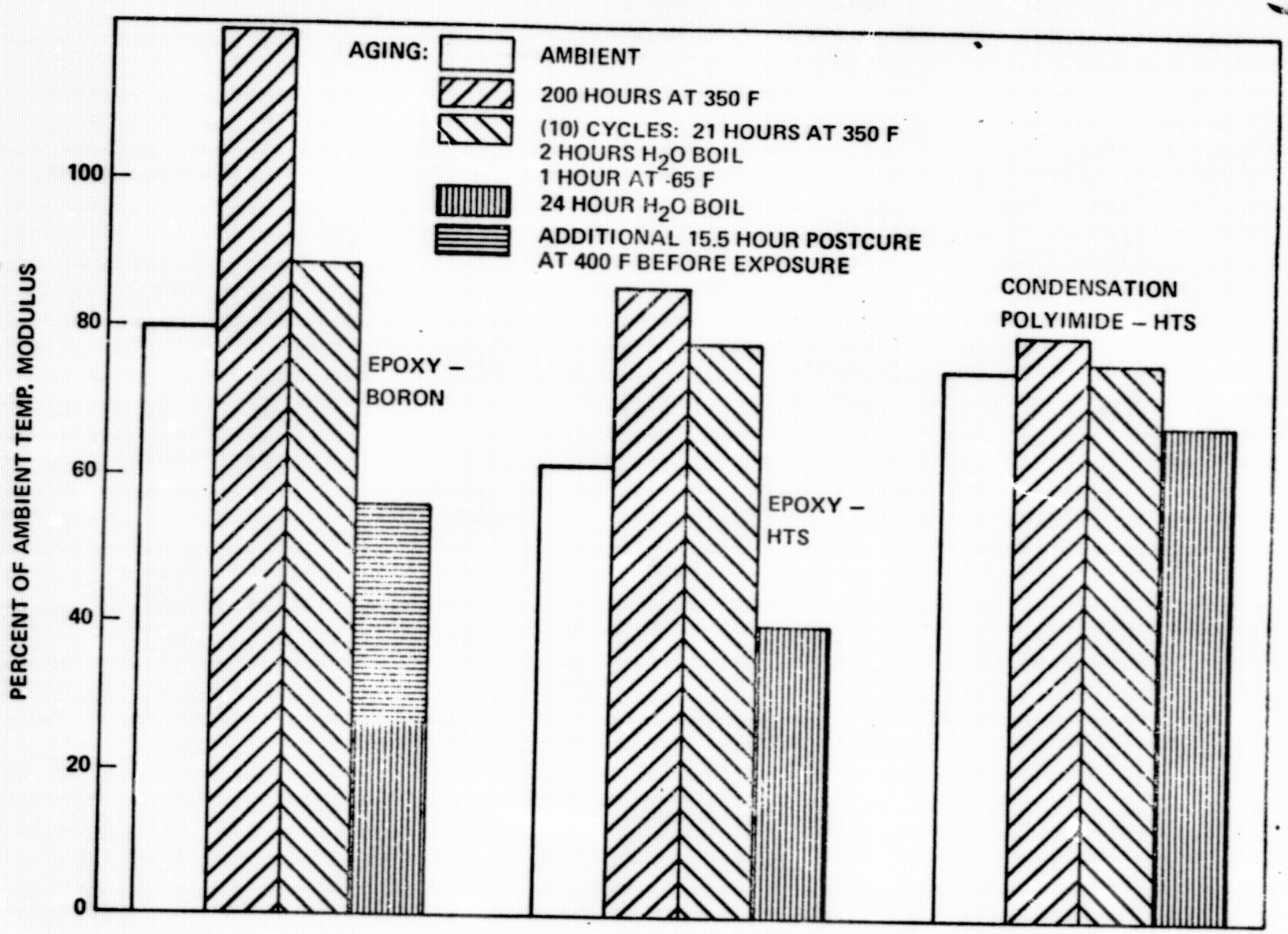
- o PHYSICAL/MECHANICAL PROPERTIES
  - QUALITY GLASS LAMINATE EASILY IDENTIFIED
  - PI LAMINATES ARE "TOUGH"
  - GRAPHITE/PI BETTER THAN EPOXY ON MOISTURE EXPOSURE
- o OTHER COMMENTS
  - FM-34 PRIMER ON Ti AND H/C CORE DEVELOPED GOOD PROPERTIES
  - COND. PI RESIN CAN BE USED FOR FORMULATING SYNTACTIC FOAM
  - ASSOCIATED PROCESSING MATERIALS ARE STATE-OF-THE-ART



EFFECT OF ENVIRONMENT ON LAMINATE FLEXURAL STRENGTH

(TESTED AT 350°F)

Tulsa Division
Rockwell International



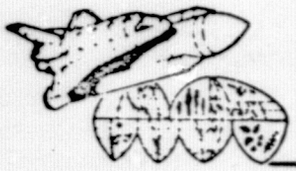
EFFECT OF ENVIRONMENT ON LAMINATE FLEXURAL MODULUS

(TESTED AT 350°F)

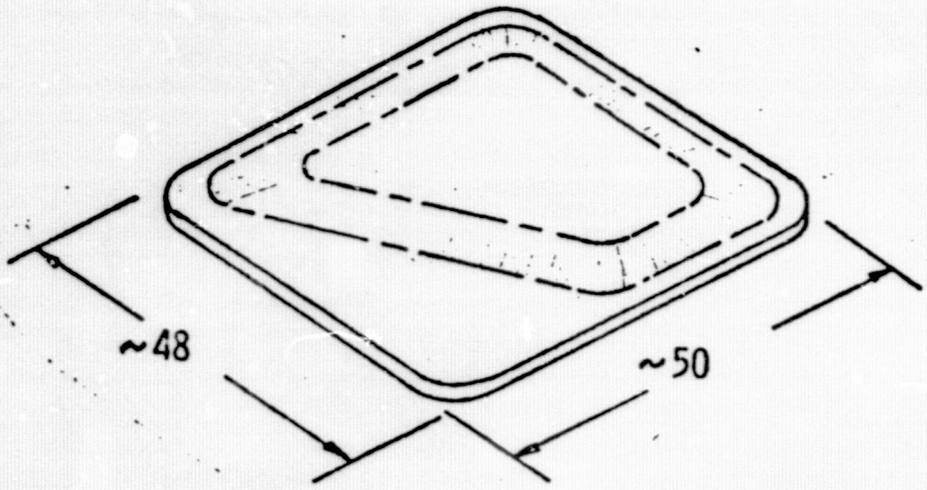
Tulsa Division
Rockwell International

POSSIBLE APPLICATION OF ADVANCED COMPOSITES

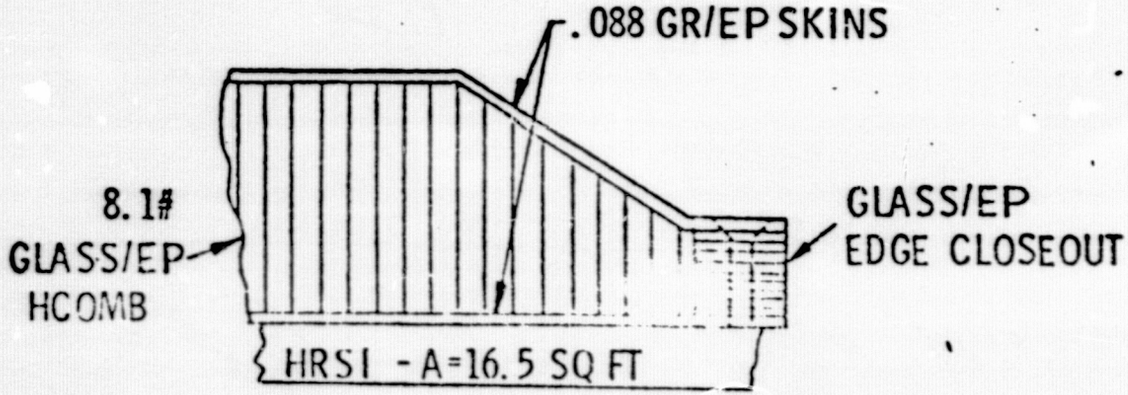
ITEM	MATERIAL	WT. SAVING, LBS.
o MLG DOORS	GR/PI (500°F)	144
o CARGO BAY DOORS GR/EP (350°F)	GR/PI (600°F)	110
o ET UMB. DOOR	GR/EP	68
o BASE HEATSHIELD	GR/EP	210
o FLOOR PANELS, PANES, & BEAMS	GR/EP	77
o ELEVONS	GR/PI (500°F)	708
o VERTICAL STABILIZER	GR/PI (500°F)	681
o THRUST STRUCTURE	DELTA II TI-BO/AL	400
o WING/GLOVE FAIRING	GR/EP	119
o RCS DOORS	GR/EP	57
o AFT BODY PANELS	GR/EP	292

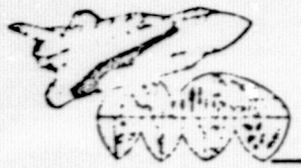


ORBITER/ET UMBILICAL DOOR

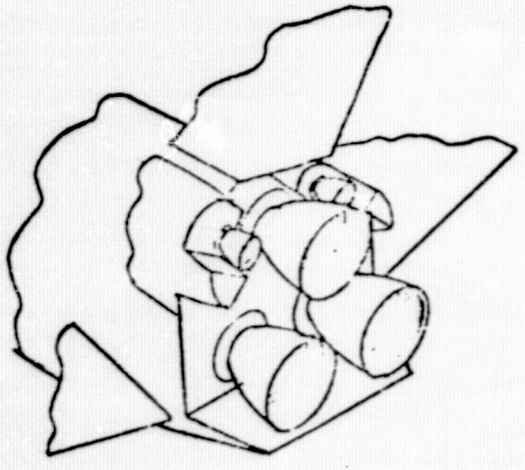


- CURRENT ALUM WT 205 LB
  PROPOSED GR/EP 137 LB
  Δ TPS, TCS —
  NET Δ WT -68 LB
- EFFECTIVITY VEH 103 & SUBS



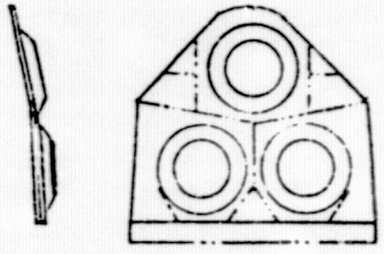


BASE HEAT SHIELD



- USE GR/EP FACE SHEETS IN PLACE OF ALUM.

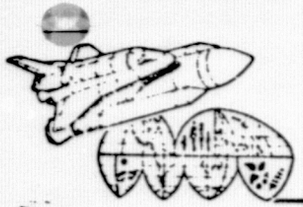
EXISTING DESIGN

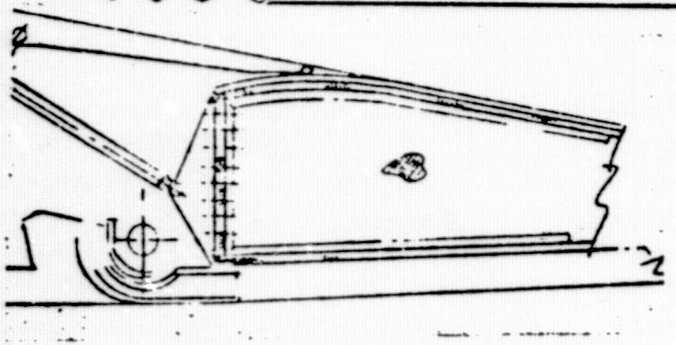


- CURRENT STRUCT. WT = 1050 LB
  PROPOSED DESIGN 840 LB
  Δ TPS —
  NET Δ WEIGHT 210 LB

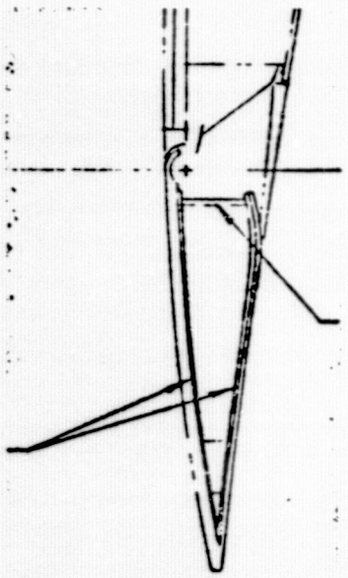
- EFFECTIVITY, VEH. 103 & SUBS

COMPOSITE INBOARD ELEVON

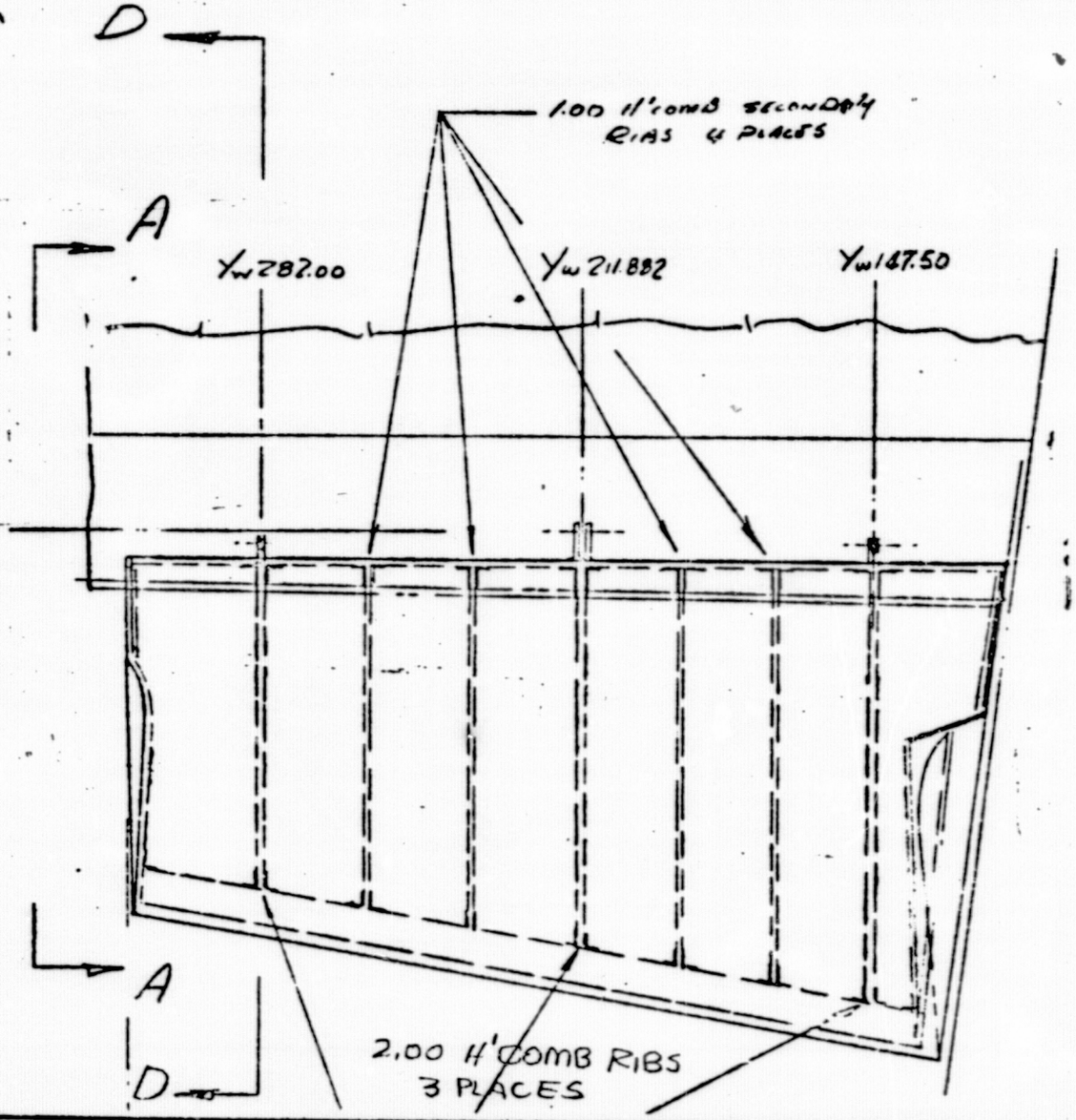




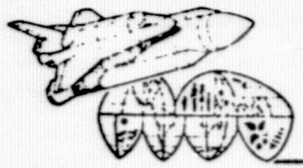
SECT D-D

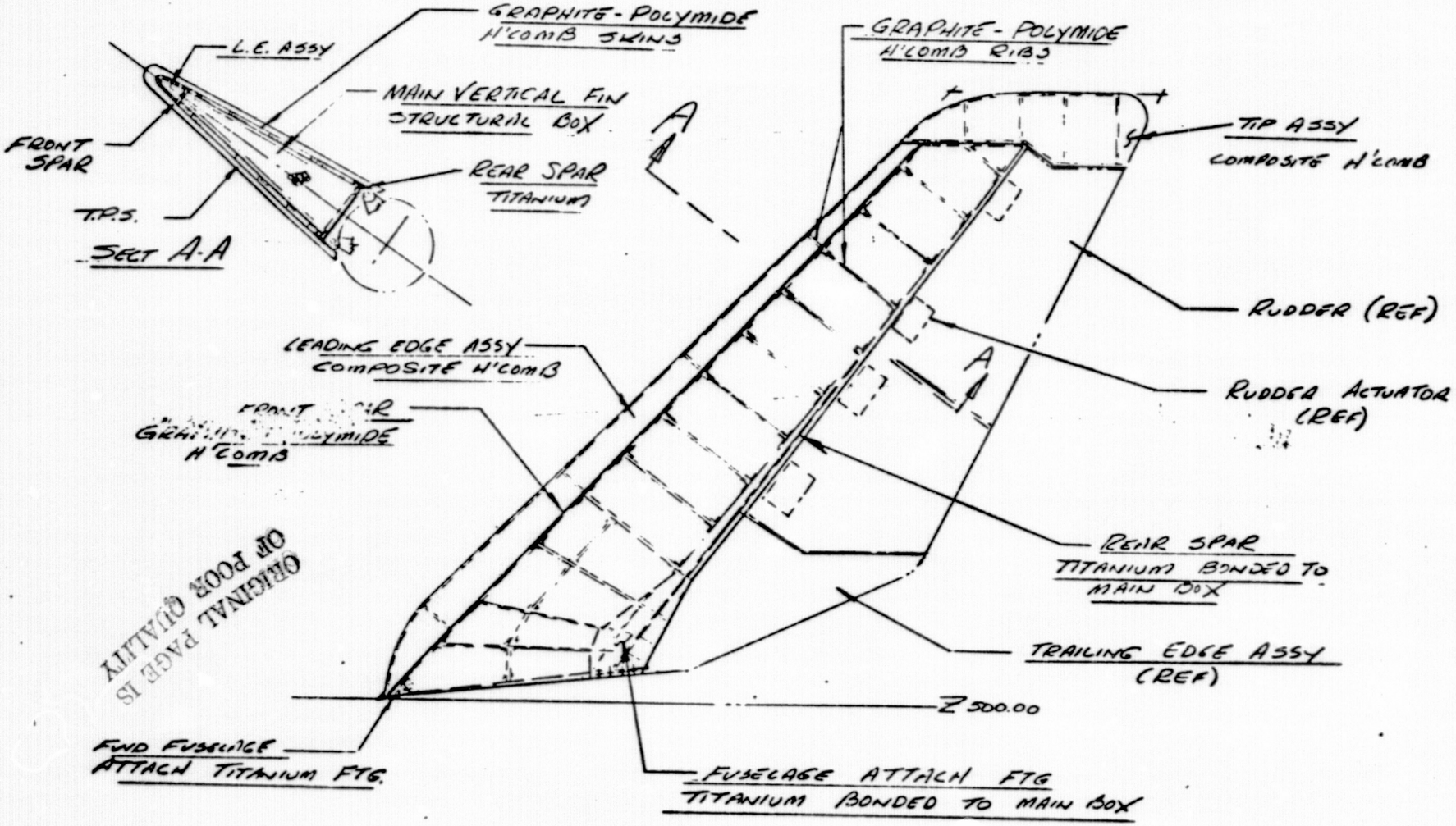


VIEW A-A



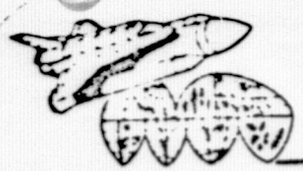
COMPOSITE VERTICAL FIN DES CONCEPT
(GR/PI)

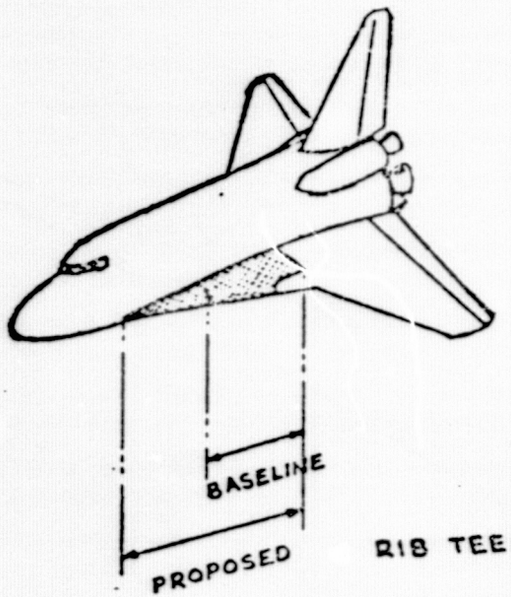


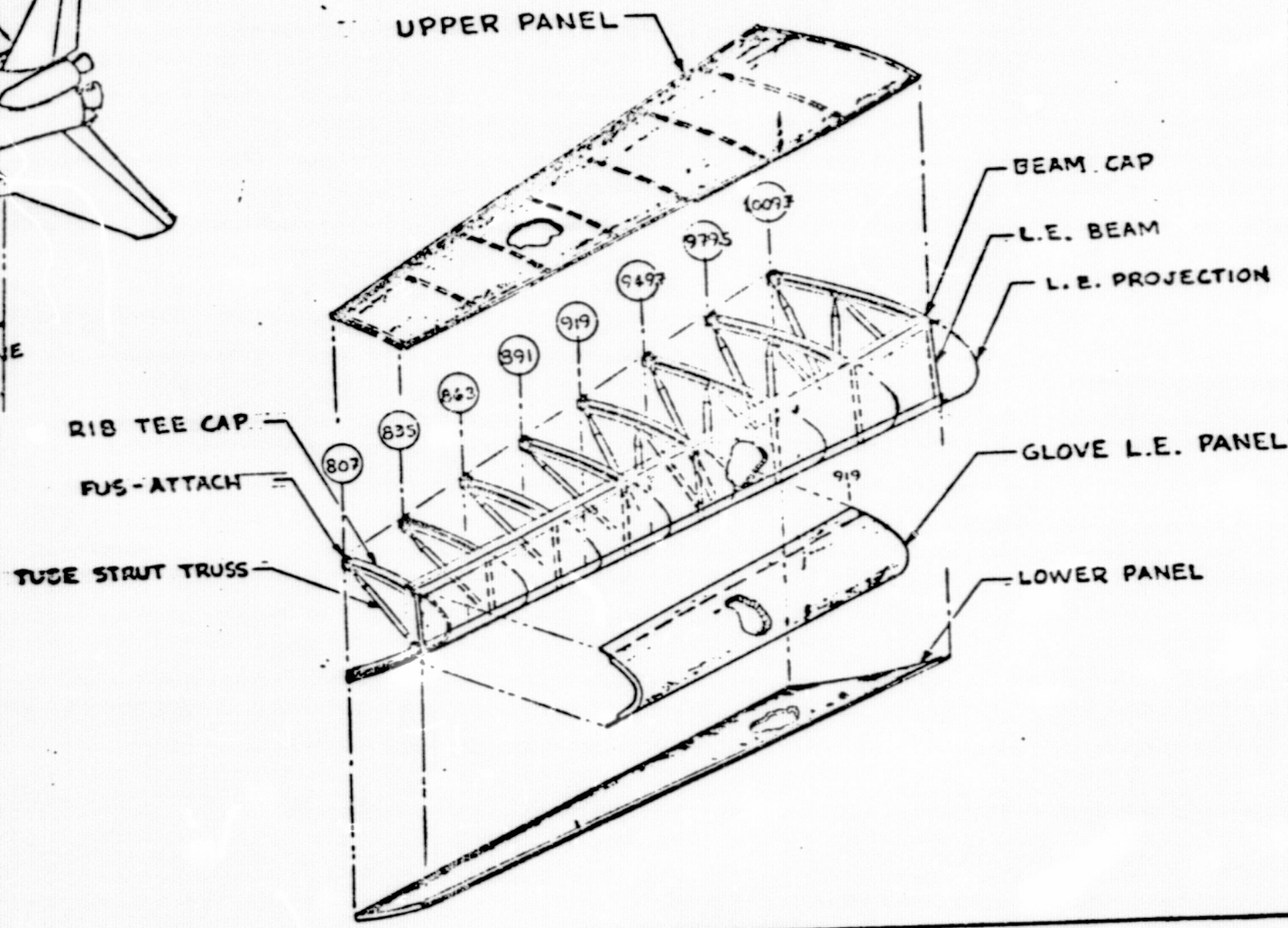


ORIGINAL PAGE IS OF POOR QUALITY

CURRENT WING/BODY FAIRING





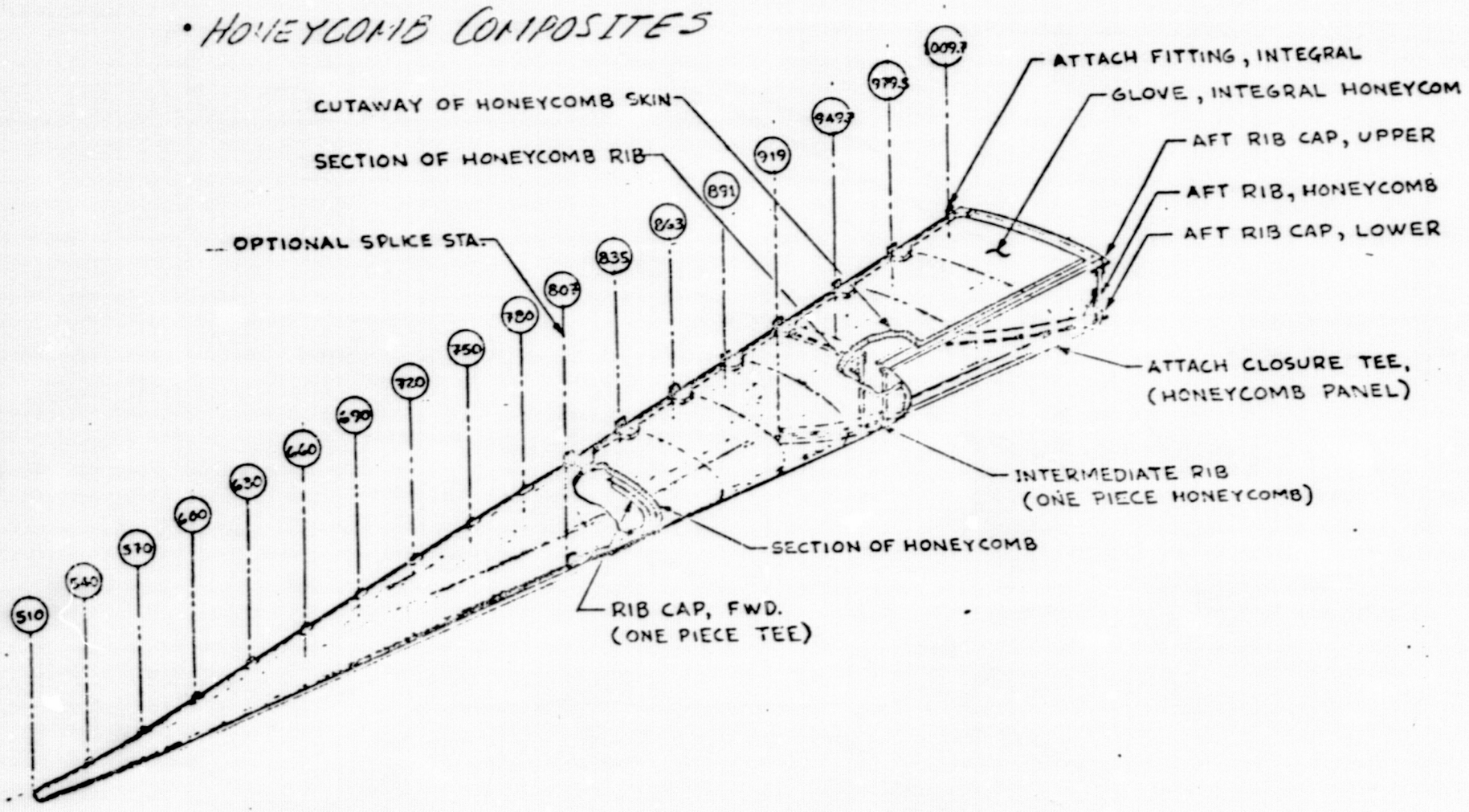


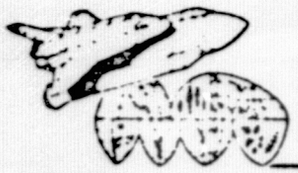
North American
Aerospace Group

Space Division
Rockwell International

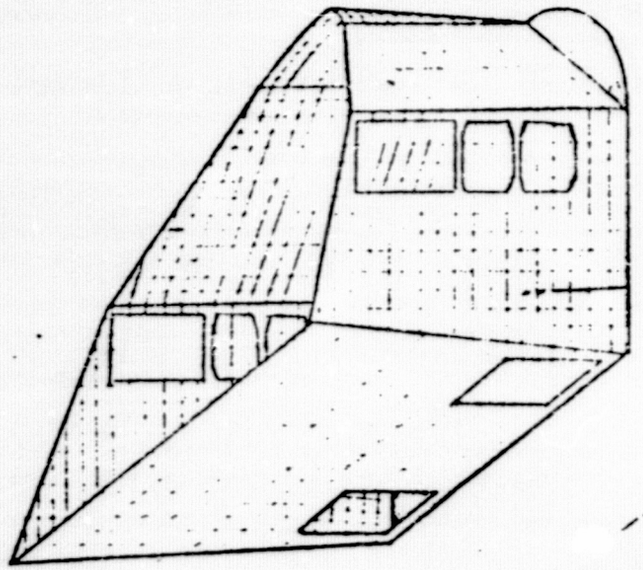
INTEGRAL WING/BODY FAIRING & GLOVE

- HONEYCOMB COMPOSITES



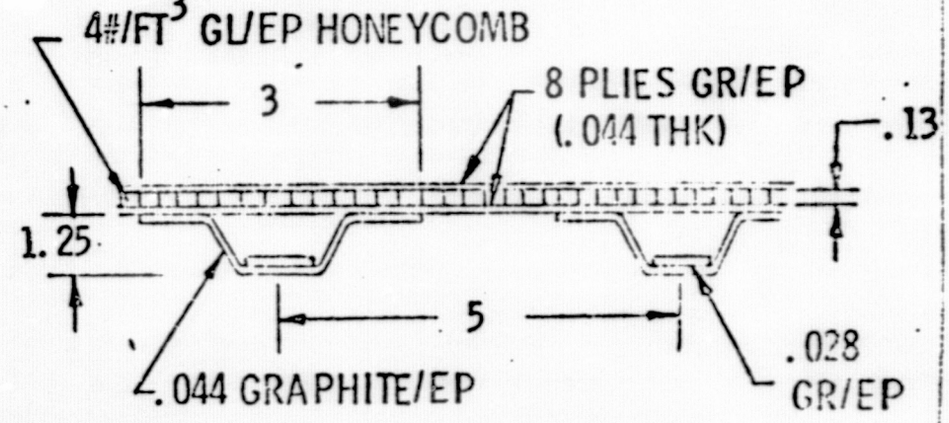


AFT BODY PANELS



- CURRENT ALUM. WT. : 1837 LB
  PROPOSED GR/EP : 1557 LB
  Δ TPS : —
  NET Δ WEIGHT : −280 LB
- EFFECTIVITY, VEH. 103 & SUBS

TYPICAL CONSTRUCTION



PLANNED ACTIVITIES

- FABRICATE HALF SECTION OF AFT BODY FLAP
- EVALUATE PROPERTIES OF HX-580/THIN-WOVEN GRAPHITE
- FABRICATE & TEST SELECTED STRUCTURE FROM HX-580/GRAPHITE
- EVALUATE PI ADHESIVE SYSTEMS FOR PI COMPOSITE JOINTS
- CONTINUE INVESTIGATIONS ON AVAILABLE POLYIMIDE RESIN & GRAPHITE FIBER COMBINATIONS FOR FUTURE USE ON SHUTTLE & OTHER AEROSPACE VEHICLES
- EVALUATE PROPERTIES OF HYBRID COMPOSITE MATERIALS

UNIDIRECTIONAL	GRAPHITE FIBER & FABRIC
WOVEN	KEVLAR FIBER & FABRIC
	COMBINATION OF ABOVE

- LOW COST POLYIMIDE CORE DEVELOPMENT
- CONTINUE STUDIES ON TITANIUM

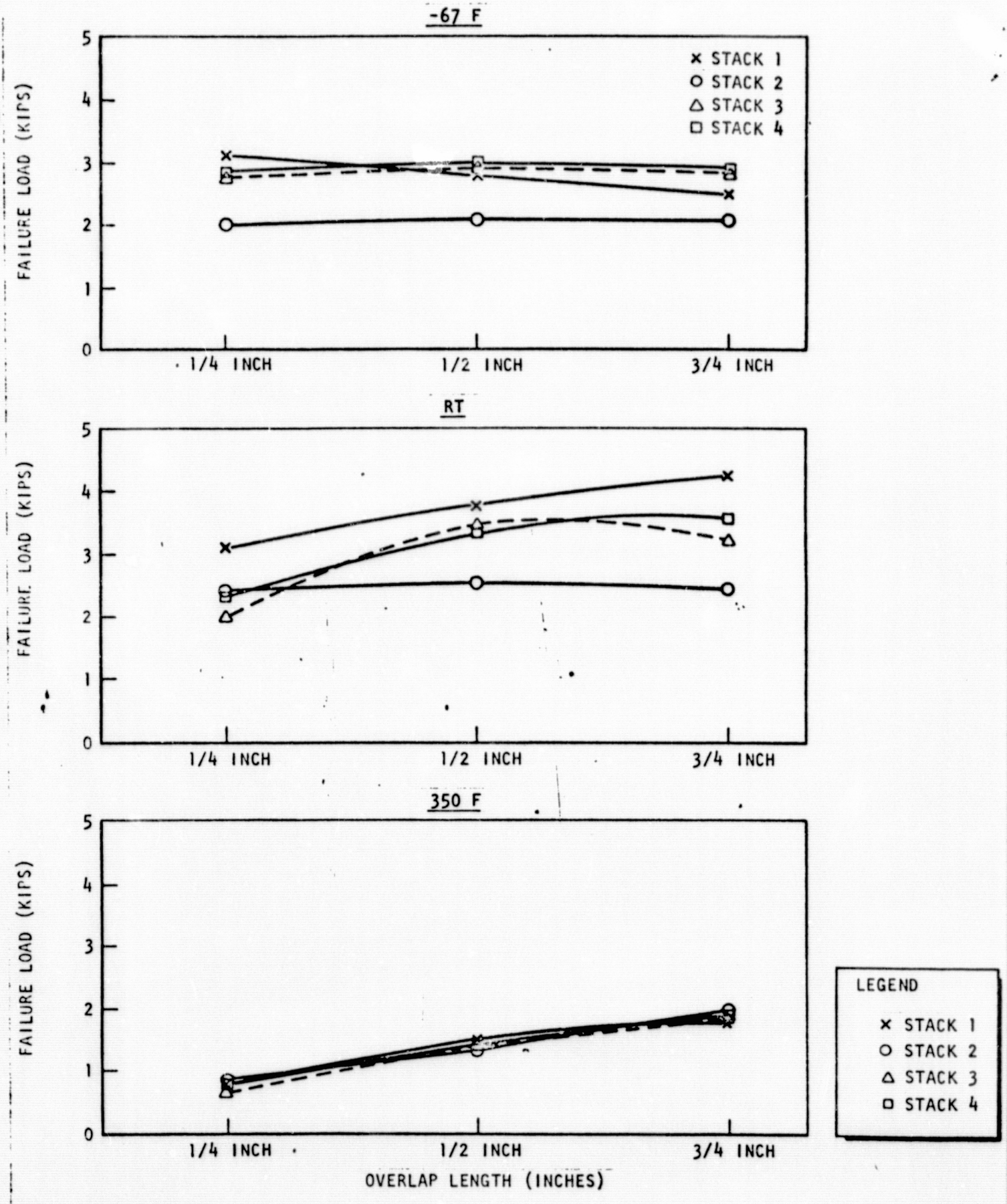
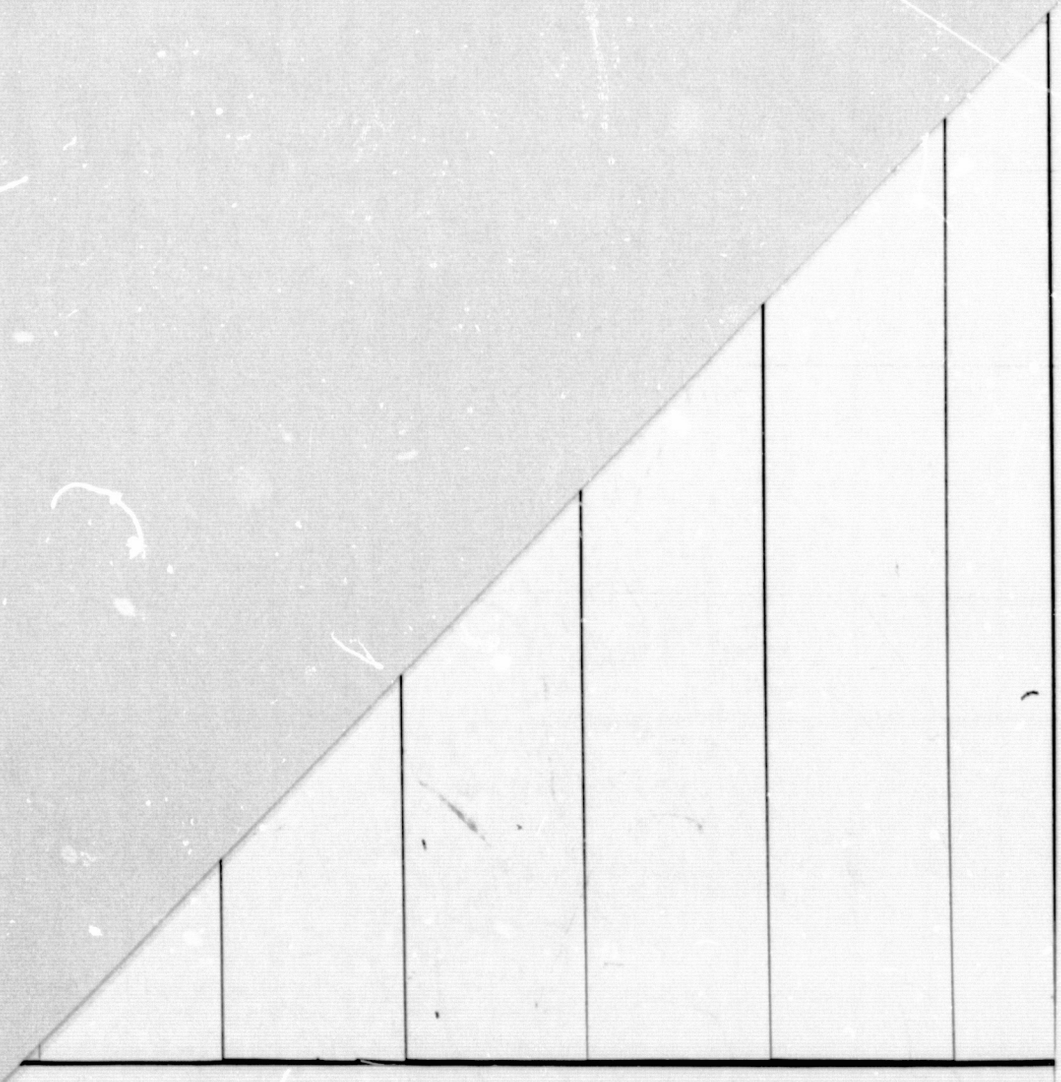


Figure 14. Summary of Total Failure Load Versus Overlap Length at Various Temperatures

TRW EQUIPMENT PRESENTATION



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PMR POLYIMIDES - PROCESSABLE HIGH TEMPERATURE COMPOSITE MATRIX RESINS

W. E. Winters - TRW Equipment, Cleveland, Ohio
T. T. Serafini - NASA-Lewis Research Center

E-3267

Abstract

Processing reproducibility and versatility were demonstrated for producing addition-cured polyimide/graphite fiber composites using a unique in situ polymerization of monomeric reactants directly on the fiber surface. The polymers so derived, designated PMR polyimides, can be fabricated into composite structures by laminating, random fiber molding or autoclave curing. Composites were determined to be thermally stable and retain useful properties after extended exposures at 550°F to 650°F. The material and fabrication capability were demonstrated by the fabrication and evaluation of prototype complex fan blades.

1. INTRODUCTION

Advanced fiber composites are becoming accepted as engineering materials for aeronautical and aerospace structural applications. The most widely used matrix materials are epoxy resins. The relatively low use temperature of epoxy resins has restricted the application of epoxy resin/fiber composites to temperatures below 350°F. Also, environmental effects on high temperature mechanical properties have restricted their application even further. High temperature resistant polymers, that is, polymers capable of withstanding temperatures up to 600°F for extended time periods, have been available since the early 1960's. However, because of their intractable nature, their potential as matrix resins has not been realized.

In 1968 investigators at the Systems Group of TRW Inc., under NASA sponsorship, developed an approach to prepare polyimides by means of an addition-reaction(1). Low molecular weight amide-acid prepolymers end-capped with norbornene rings were found to polymerize without the evolution of volatile material.

Studies conducted at the NASA-Lewis Research Center led to the development of a vastly improved method for preparing addition-cured polyimides(2),(3). In this approach, in situ Polymerization of Monomer Reactants occurs on the surface of the reinforcing fibers. The polymers derived using the techniques are designated PMR polyimides.

Studies reported in references (4) and (5) were undertaken by TRW Equipment

C-5

of TRW Inc. to establish a broad technology base for PMR polyimides. These studies included work to define PMR polyimide/graphite fiber processing methodology and the characterization of composite mechanical property retention characteristics at elevated temperatures over extended time periods. This work culminated in the fabrication of complex fan blades designed for operation at blade tip speeds of 2200 ft/sec.

This report reviews the PMR polyimide composite studies conducted at the NASA-Lewis Research Center and TRW Equipment. Particular emphasis is given to the recent studies[5][6] which describe the processing versatility and use of PMR polyimides to fabricate composite fan blades.

2. MATERIALS

Aromatic polyimides are generally formed by the reaction of aryl diamines with aromatic dianhydrides or the dimethyl esters of aromatic tetracarboxylic acids. Following impregnation of reinforcing fibers with a "polyimide varnish" solution, mild heating (staging) of the prepreg, to achieve an acceptable level of volatiles, results in the formation of molecular structures which adversely affect the removal of volatile materials produced during final curing under pressure. Addition polyimides of the "A" type[1] are achieved through the polymerization of low molecular weight prepolymers end-capped with norbornene groups without the evolution of volatile materials. PMR polyimides are also cured by an addition reaction of norbornene groups. The structures of the monomers, intermediate and cured polymer are shown in Figure 1. Specifically, the reactants used to produce the PMR polyimides used in this study were as follows:

(1) 4,4'-methylenedianiline (MDA)
(2) Monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE)
(3) Dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE)

The MDA and NE are commercially available crystalline materials while the BTDE is readily obtained by refluxing the dianhydride of benzophenonetetracarboxylic acid (BTDA) in methanol. All reactants are readily soluble in anhydrous methanol at room temperature. Concentrated (25-60 w/o), low viscosity (20-60 cps) solutions which are stable for at least two weeks can be prepared. Because solution preparation merely involves simple mixing, monomer solutions can be prepared daily so that storage or shelf life problems are non-existent with PMR polyimides. Also, because of the ease of solution preparation, formulated molecular weight (FMW) variations are readily achieved. FMW's ranging from 1000 to 1900 have been studied. In general, higher molecular weight resin is characterized by lower resin flow during processing while lower FMW, having higher alicyclic content and crosslink density, exhibits somewhat lower thermo-oxidative stability and slightly greater stiffness. Following are the number of moles of the constituents used for two PMR polyimides of different FMW:

FMW	NE	MDA	BTDE
1100	2	2.260	1.260
1500	2	3.087	2.087

The majority of effort with PMR polyimides has been devoted to composites using graphite fiber reinforcements including both high strength (HT-S) and high modulus (HM-S) type fibers. However, sound (void-free) composites have been produced using "E" and "S" glass reinforcements as well.

3. PROCESSING VERSATILITY

3.1 PROCESSING PARAMETERS

The basic processing steps for producing composites of PMR polyimides are much the same as for other "A" type polyimides. However, as indicated in

Table I, a high degree of processing flexibility exists. The fiber collimation and impregnation operations are conventional except that the low viscosity solution assures total impregnation of fiber bundles and fiber wetting. Staging to reduce volatiles for appropriate tack and drape properties can be achieved at room temperature or by mild heating. Imidization can be accomplished on a pre-stacked laminate either in an air-circulating oven, in the final molding tool, or on the mandrel. Higher temperatures and longer imidization times result in reduced resin flow in final cure.

The final curing operation is performed by inserting the imidized preform in a warm or hot tool or by using a tool or mandrel equipped with heaters. One of the particularly advantageous characteristics of the material is that, with lower insertion temperatures, a reasonable amount of time can elapse before pressure application, thereby eliminating operator judgment factors. Cure is achieved in one hour at 600°F. Postcure is essential where maximum use temperature and exposure time requirements demand ultimate performance. However, unduly long or complicated programmed temperature rise schedules are not required.

3.2 PROCESSING AND FMW EFFECTS

The selection of a resin matrix system for a complex hardware configuration of composite material is dependent not only on the ability of the resin matrix to translate fiber efficiency and achieve the required resistance to thermal degradation, but upon the ability of the material to be fabricated into a sound structure with reasonable ease. Some applications and processing methods demand more resin flow to achieve full composite consolidation than do others. The versatility of FMW variation in PMR polyimides allows a wide range of resin flow. Figure 2 shows that 20% resin expulsion occurs at an FMW of 1000. Some loss in thermo-oxidative stability of lower molecular weight polymers is exhibited at 550°F (Figure 3) while at 450°F insignificant loss in weight is observed to at least 600 hour exposure.

The variation of composite flexural strength (normalized for 0.55 V_f) with molecular weight using HT-S graphite fiber is illustrated in Figure 4. Room temperature strength ranged from 223 ksi at FMW of 1000 to 200 ksi at FMW 1500. Retention of strength at 450°F ranged from 75 to 88% and at 550°F from 70-78%. Elevated temperature tests were conducted after 15 minutes exposure at the indicated temperatures.

It is interesting to note in Figure 4 a decrease in strength at higher molecular weight levels. It is felt that the data reflect the effect of matrix modulus as well as temperature. The lower FMW, having a higher alicyclic, higher cross link density would be expected to exhibit a higher neat resin modulus and lower thermal stability. The room temperature results thus reflect the effect of matrix modulus while the elevated temperature strengths reflect both matrix modulus and temperature effects.

3.3 FABRICATION METHODS

Fabrication of PMR polyimide composites by compression molding or conventional laminating techniques is straightforward and reproducible. A pre-imidized stack or preform is inserted into a closed die or heated platens, and after a short dwell period to assure through-heating, pressures of 500 to 1000 psi are applied. The high melt viscosity of higher FMW formulations preclude fiber wash or excess resin expulsion.

Although most of the composite fabrication to date has been by closed die molding of continuous fiber composite, other approaches also have been investigated. A highly successful method has been random fiber molding using a chopped graphite fiber/PMR-15 molding compound. In this case, collimated fiber prepreg was merely chopped to the

desired fiber length. Figure 5 illustrates a 2-3/4 inch diameter puck molding with legs of varying size which is used to investigate the fiber/resin flow characteristics of the material. In this case, only the smallest (1/4 inch diameter) of the three legs did not completely fill. Distribution of resin and reinforcement was, however, excellent in all cases. The photomicrograph of the body of the puck illustrates a completely void-free structure while the mechanical properties are typical of a good quality molding compound incorporating 3/8 inch lengths of high strength graphite fiber.

Another fabrication approach for which feasibility has been demonstrated with PMR polyimides is autoclave curing. Figure 6 illustrates two typical photomicrographs of autoclave cured (200 psi) unidirectional graphite composites indicating a void content of 2.7%. It will be noted that the porosity is primarily interply suggesting entrapped air rather than reaction by-product volatiles. Optimization studies are continuing through cure schedule and FMW modifications and there is high confidence that even lower void content composites can be reproducibly achieved.

The addition type polymerization mechanism of PMR polyimides coupled with extended gellation times and available resin flow permit fabrication of composites of essentially unlimited thickness. Figure 7 illustrates a fully dense, half-inch thick laminate. Both unidirectional and oriented composites of this dimension and thicker have been produced without difficulty. It is concluded that PMR polyimides are adaptable to a variety of fabrication methods and hardware applications.

4. COMPOSITE PROPERTIES

The evaluation of PMR polyimide composites made from PMR-15 (polyimide of FMW = 1500) has been extensive. In general, excellent translation of fiber properties is achieved with retention of properties for extended air aging up to 600°F. Particular emphasis has been placed on effects of processing on mechanical performance. Table II presents room and short term 600°F properties for two distinctly different processing conditions. The insertion temperature refers to the tool or platen temperature into which the imidized preform is charged. Essentially, no difference in properties is observed between the two methods. The need for postcure to achieve best 600°F properties is dramatically evident. However, for application at lower temperatures (e.g., 450°F), large percentages of the room temperature properties are retained without the need for postcure as illustrated in Table III.

Long term, elevated temperature aging effects in air environment are demonstrated in Figure 8. At 550°F fully postcured HM-S graphite composites experience essentially no thermo-oxidative degradation for durations of at least 1000 hours while at 600°F the weight loss is significant but not excessive. Serious degradation is experienced with extended air exposure at 650°F. Relating weight loss to mechanical performance, 60-80% of the unaged flexure strength is retained after 600°F/1000 hours exposure. At 650°F composites maintain 90% of their strength at 50 hours exposure indicating that short duration excursions to higher than normal or desired temperature ranges would not be catastrophic to a composite structure.

5. HARDWARE APPLICATION

One of the most rewarding aspects of the PMR polyimide development has been the success achieved in fabrication of prototype hardware. Selected for the demonstration was the ultra-high tip speed blade illustrated in Figure 9. This blade is perhaps the most complex, most highly loaded rotating airfoil ever developed. The design was created by

Pratt and Whitney Aircraft, East Hartford, Connecticut under Contract (NAS3-15335) from NASA-Lewis; the tooling and fabrication development were conducted at TRW Equipment.

The purpose of the blade program is to investigate the aerodynamics of airfoil designs at speeds never before evaluated. The blade rotates at over 15,000 rpm at tip speeds of 2200 ft/sec. Because of the very high stresses involved in the centrifugal and aerodynamic fields, no homogeneous material could survive and the use of high specific strength and stiffness resin composites was mandatory.

The blade is about eleven inches long and eight inches in chord at the tip. Composite thickness varies from over one-half inch at the root to about 0.022 inch at the leading edge. The reinforcement is HT-S graphite fiber and the construction is of varying fiber orientations to achieve the required radial and torsional strengthening and stiffening. The composite structure consists of 77 plies of five and 10 mil material in a complex arrangement of computer developed ply shapes. The root is a splayed fiber construction with metallic wedges and pressure pads.

The blades were compression molded in a simply constructed but complex configured closed die fabricated to close tolerances. The tool was mounted in a hydraulic platen press capable of applying 800 psi on the 75 in^2 of projected blade area. Imidization was conducted in the tool and the fully imidized preform was molded using the 450°F insertion cycle described earlier.

To date, six of these blades have been produced using PMR-15 polyimide resin matrix. The fabrication was straightforward and no difficulties were encountered using the imidization and cure schedules developed on flat laminates.

The prepreg used in the blade fabrication was prepared by drum winding with careful control of ply thickness. Since dimensional tolerance of thickness on the finished item is approximately $\pm$ 1%, extreme ply thickness control was essential. Although low resin flow was obtained in the molding operation, the reproducibility of final blade weight and thickness was excellent. Post-mold evaluation by ultrasonic C scan and radiography indicated a sound composite structure.

Several of the blades were spin tested singly in a counter balanced wheel. One blade survived a particularly harsh set of testing conditions. After incremental excursions up to full speed with ultrasonic evaluation after each increment, the blade was subjected to low cycle fatigue (LCF) by spinning up to 100% speed fifty times. This was followed by ten million cycles in high cycle fatigue in first bending mode. Finally, an additional ten cycles in LCF were performed prior to final evaluation. The blade after test was intact although some amount of delamination and cracking had been experienced.

As a result of the success achieved with a limited number of blade trials with a new material, the PMR type polyimide has been selected as the bill-of-material. The program is continuing with additional blade development and design optimization. Ultimately, sufficient blades will be fabricated for a single wheel-set which then will be evaluated for aerodynamic performance.

6. CONCLUDING REMARKS

The in situ polymerization of monomer reactants (PMR) approach to producing polyimide polymers has been demonstrated to be a viable concept for generating composite structures exhibiting superior high temperature properties, lower cost and greater safety. Of particular advantage are the ease of resin preparation, low viscosity solutions assuring reinforcement wet-out, and a variety of cure schedules which are

independent of operator judgment. The readily prepared compositions can be tailor made to a particular requirement or processing method. Fabrication approaches which can be used include lamination, random fiber molding and autoclave curing. The PMR approach has been demonstrated to be capable of producing highly sophisticated hardware of high quality and PMR polyimides can be considered at this time as available engineering materials of construction.

REFERENCES

1. Burns, E. A., Lubowitz, H. R., Jones, J. F., "Investigation of Resin Systems for Improved Ablative Materials," NASA Report No. CR-72460, October 1968.

2. Serafini, T. T., Delvigs, P., and Lightsey, G. R., "Thermally Stable Polyimides from Solutions of Monomeric Reactants," J. Appl. Polym. Sci., Vol. 16, No. 4, April 1972, pp. 905-915.

3. Delvigs, P., Serafini, T. T., Lightsey, G. R., "Addition-Type Polyimides from Solutions of Monomeric Reactants," NASA Technical Note TN D-6877, August 1972.

4. Cavano, P. J., "Resin/Graphite Fiber Composites," NASA CR-121275, March 1974.

5. Cavano, P. J., "Resin/Graphite Fiber Composites," NASA CR-134727, December 1974.

6. Serafini, T. T. and Vannucci, R. D., "Tailor Making High Performance Graphite Fiber Reinforced PMR Polyimides," NASA TM X-71616, 30th Symposium, Soc. Plastics Industry, Wash., D.C., February 1975.

BIOGRAPHIES

Mr. William E. Winters received the Bachelor of Science degree in Chemical Engineering at Case Institute of Technology which has been augmented with graduate work in polymers and composites. He is the Section Manager of the Resin Composites Section in the Materials Technology Department of TRW Equipment, Cleveland, Ohio. Experience includes over 15 years in ablative and structural composite materials and process development.

Dr. Tito T. Serafini is presently Head of the Polymer Matrix Composite Section of the NASA-Lewis Research Center where he has been since 1963. He received his B.S. in Chemical Engineering, M.S. and Ph.D. from Case Institute of Technology; was a member of the Case Staff in 1961 and received a post-doctoral fellowship from the University of Turin (Italy) in 1962. His current research is in the areas of polymer synthesis and composite fabrication and characterization.

TABLE I

BASIC PMR COMPOSITE PROCESSING

1. Collimation and Impregnation
   - 50% Solids Solution
   - Air or IR Dry
   - Oven Stage to Desired Tack/Drape

2. Imidize
   - Oven or Tool
   - Temperature 250° to 400°F
   - Time 1 to 3 hours

3. Mold
   - Insert Preform Hot 450° to 600°F
   - Dwell 30 seconds to 10 minutes
   - Pressure 200 to 1000 psi
   - Cure Temperature 600°F
   - Time 1 hour

4. Post Cure
   - Temperature 650°F
   - Time 16 hours

TABLE II

COMPOSITE PROPERTIES VS. PROCESSING CONDITIONS
MATERIAL: PMR-15/HM-S

Processing Insertion Temperature Dwell Post Cure	450°F 10 min None	450°F 10 min 650°F/16 hr	600°F 30 sec None	600°F 30 sec 650°F/16 hr
Properties at Room Temperature				
Flexure Str., ksi	196	-	183	-
Flexure Mod., msi	25.5	-	26.9	-
Shear Str., ksi	8.8	-	8.5	-
at 600°F				
Flexure Str., ksi	-	134	70	160
Flexure Mod., msi	-	22.1	15.2	25.2
Shear Str., ksi	-	6.6	3.2	6.4

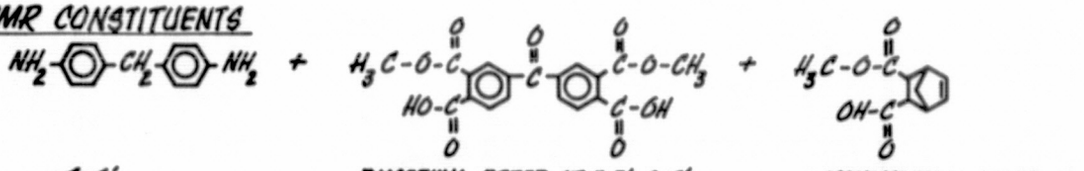
TABLE III

ELEVATED TEMPERATURE PROPERTIES OF
NON-POSTCURED PMR-15/HT-S LAMINATES

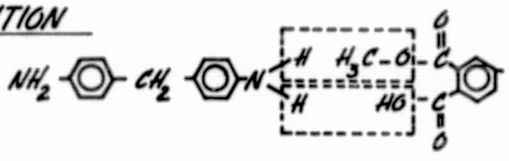
	72°F	450°F	% of Retention
Flexure Strength, psi	248,700	189,800	76%
Flexure Modulus, psi	18.1×10^6	16.9×10^6	93%
Shear Strength, psi	16,300	9,000	55%

PMR CHEMISTRY

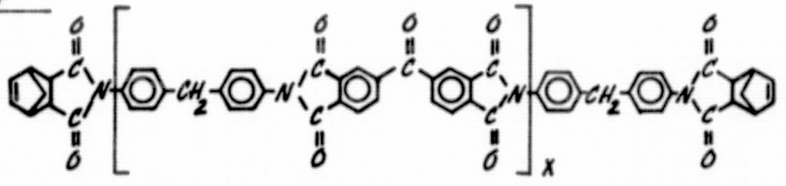
PMR CONSTITUENTS



IMIDIZATION REACTION



AFTER IMIDIZATION



REPEATING UNIT

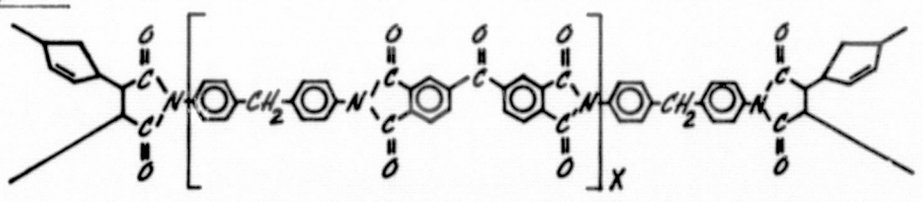


Figure 1. - PMR polyimide chemistry.

E-8267

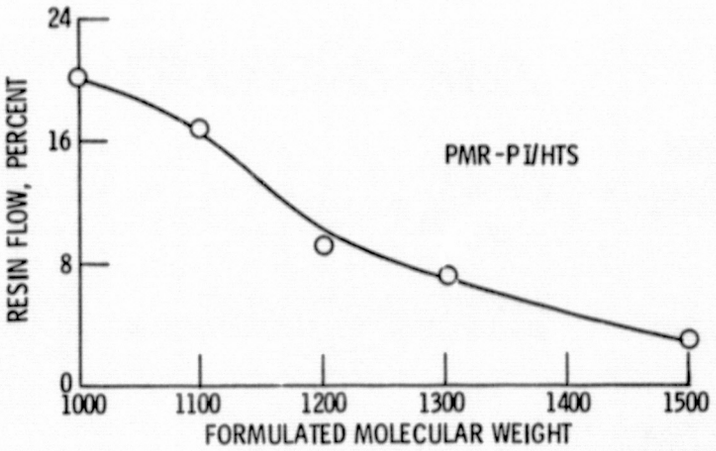


Figure 2. - Percent resin flow vs. formulated molecular weight.

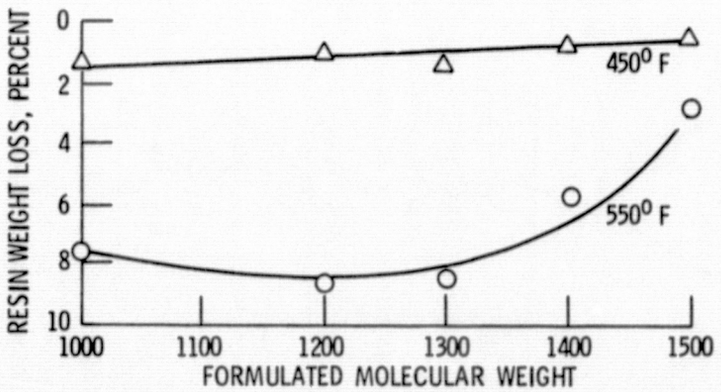


Figure 3. - Isothermal resin weight loss of PMR-PI/HTS composites exposed for 600 hr. in air vs. formulated molecular weight.

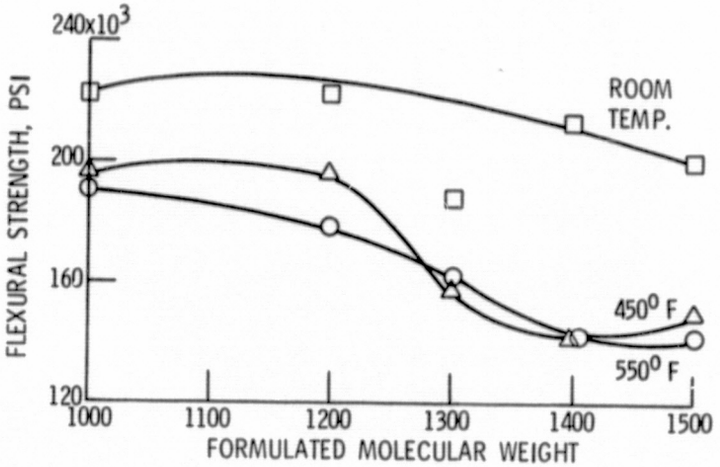
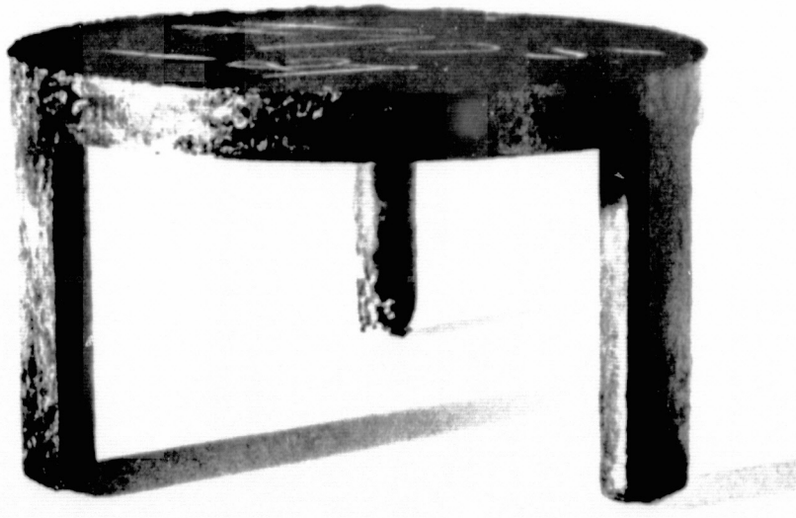


Figure 4. - Flexural strength of PMR-PI/HTS composites. Tests conducted at room temperature and at 450° and 550° F after short-time exposure at indicated test temperature.

E-8267

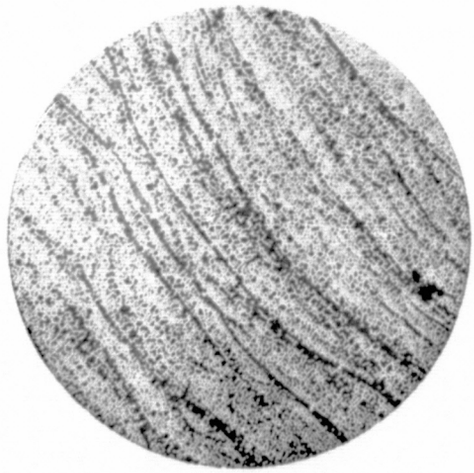


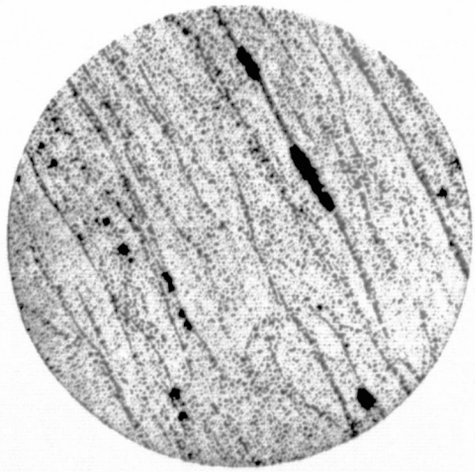


PROPERTIES:	FLEXURE STRENGTH	40 000 PSI	FIBER:	LENGTH	3/8 IN.
	FLEXURE MODULUS	4×10^6 PSI		LOADING	57.5 V/O
	TENSILE STRENGTH	15 000 PSI			

Figure 5. - PMR-15/HT-S random fiber molding.

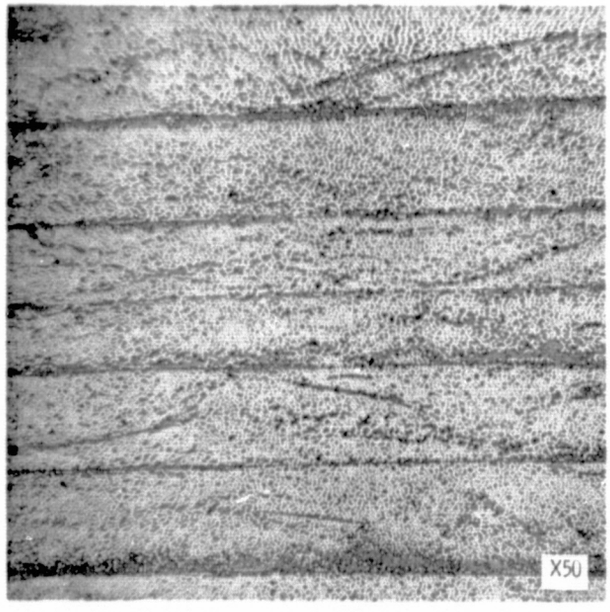
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FLEXURE STRENGTH	152 300 PSI
FLEXURE MODULUS	19.3×10^6 PSI
SHEAR STRENGTH	6100 PSI
FIBER FRACTION	0.56
SPECIFIC GRAVITY	1.58
VOID CONTENT	2.7 PERCENT

Figure 6. - Properties of autoclave cured PMR-15/HM-S composites.



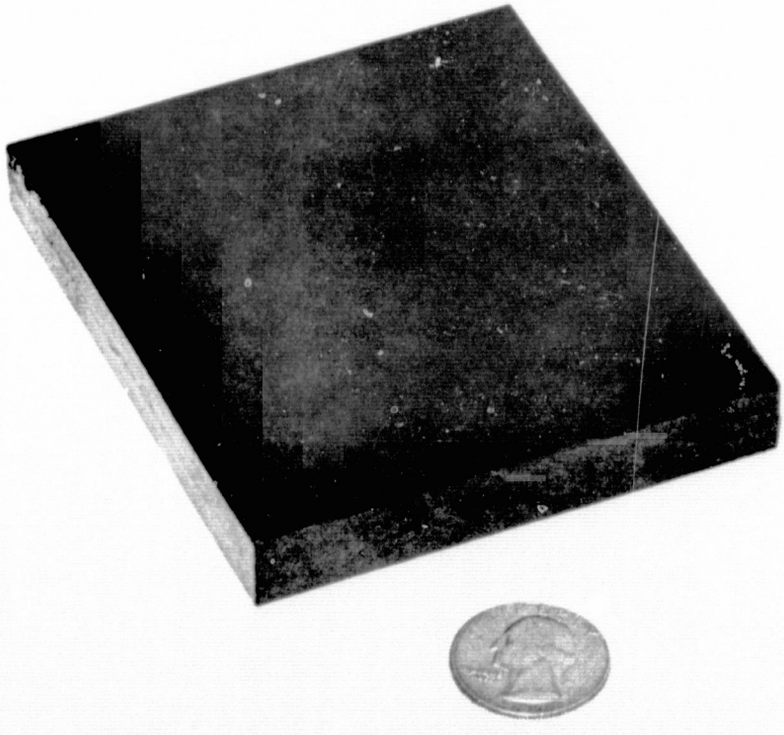


Figure 7. - PMR-15/HT-S thick laminate.

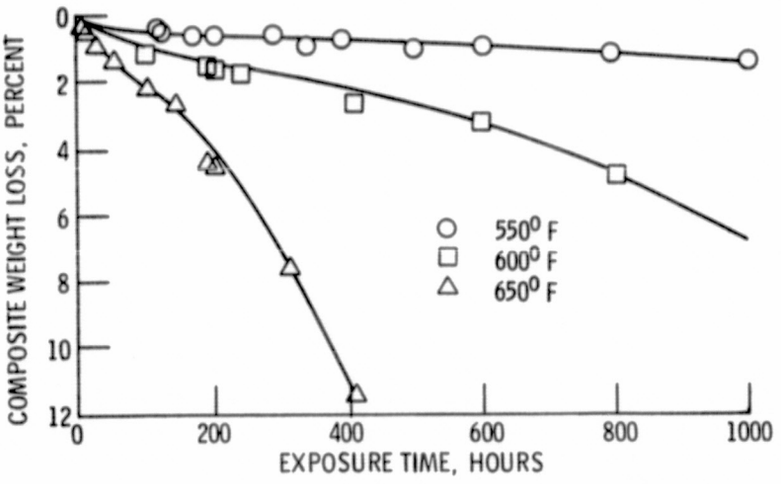


Figure 8. - Percent weight loss of PMR-15/HM-S composites exposed to 100 Ml/min air flow at temperatures shown.

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Figure 9. - PMR-15/HT-S ultra-high tip speed fan blade in finished machined form.

WHITTAKER PRESENTATION

WHITTAKER PRESENTATION

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PRESENT STATUS OF GRAPHITE/PI AND PI ADHESIVE TECHNOLOGY

A WHITTAKER R&D VIEWPOINT

M. MAXIMOVICH
Sr. Research Specialist

POSSIBLE PI CANDIDATE RESINS

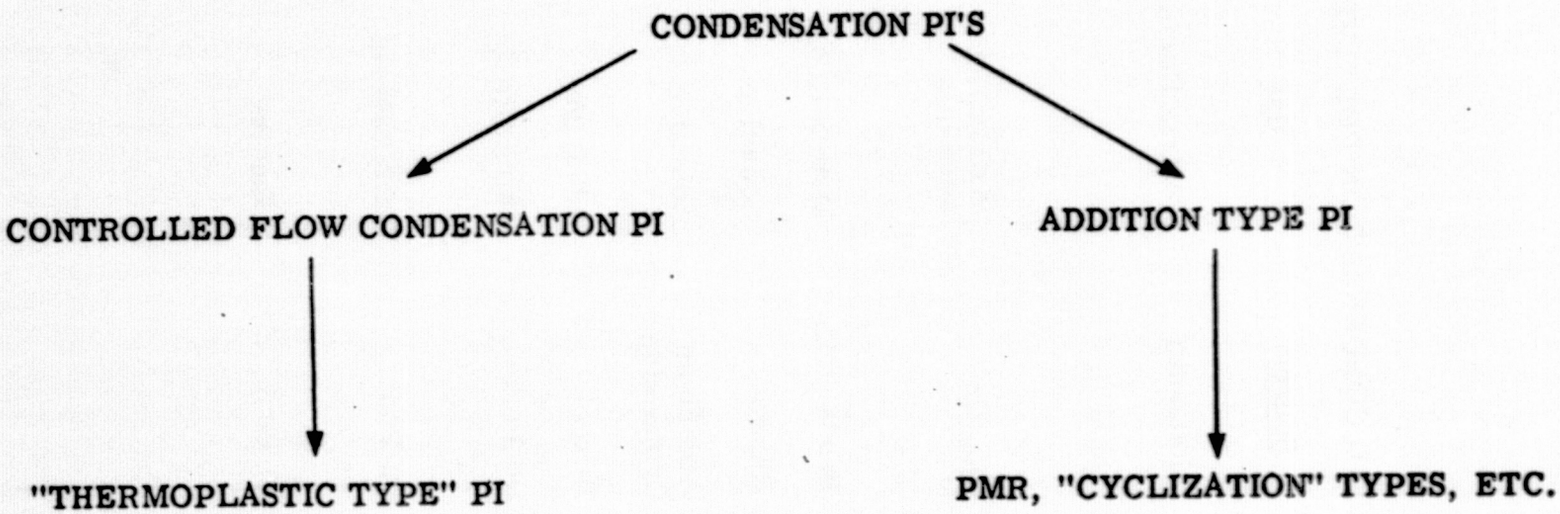
Condensation Type	Addition Type	Misc.
Skybond 700	P13N	2080
703	P105A	
709	Kerimid 601	
710	Kerimid 353	
F170→174	F175→178	
BPI 373	PMR 15	
Nolimid A380	3003	
FM 34		
951		
4701		
NR150 A		
B		
A2		
B2		
AG		

CANDIDATES WITH ESTABLISHED 600°F LONG TERM CAPABILITY

NR150B, B2

CANDIDATES WITH ESTABLISHED 600°F CAPABILITY AND PROCESSABILITY COMPATIBLE WITH PRESENT M&P FACILITIES AND STATE-OF-THE-ART PROCESSING TECHNIQUES

PI DEVELOPMENT



COMMERCIAL CONDENSATION POLYIMIDE SYSTEMS

Description	Source	Use	Product Form
Skybond 700 Skybond 703 Skybond 709 Skybond 710	Monsanto	Matrix Resin	Solution
F170 F171 F172 F173 F174	Hexcel	Matrix Resin Adhesive	Prepreg
BPI 373	Brunswick	Matrix Resin	Prepreg
Nolimid A380	Rhodia	Adhesive	Prepreg
FM-34	American Cyanamide	Adhesive	Solution, Prepreg
951	Hexcel	Adhesive	Solution, Prepreg
4701	Du Pont	Matrix Resin	Solution
NR-150A NR-150B NR-150A2 NR-150B2	Du Pont	Matrix Resin	Solution
NR-150AG	Du Pont	Adhesive	Solution

CONDENSATION PI PROBLEM AREAS

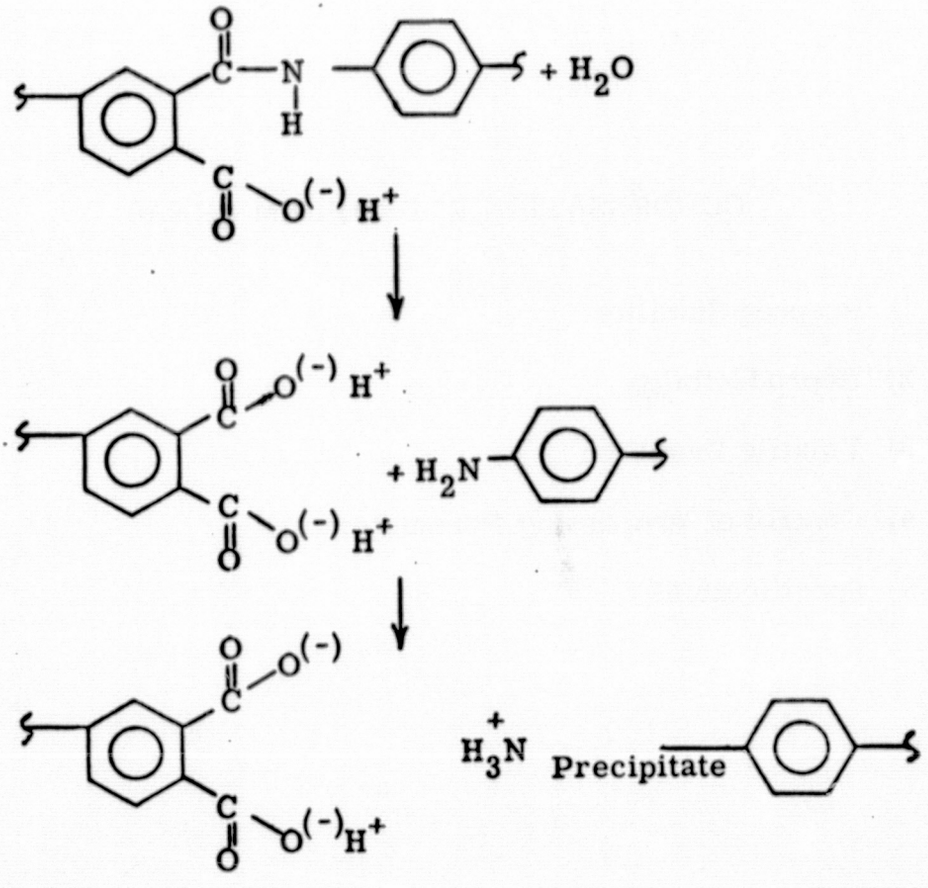
1) Prepreg Stability

2) Reproducibility

3) Volatile Evolution

4) Control of Processing Parameters

5) Specifications



TYPICAL HYDROLYSIS REACTION

MOST PROMISING CONDENSATION TYPES

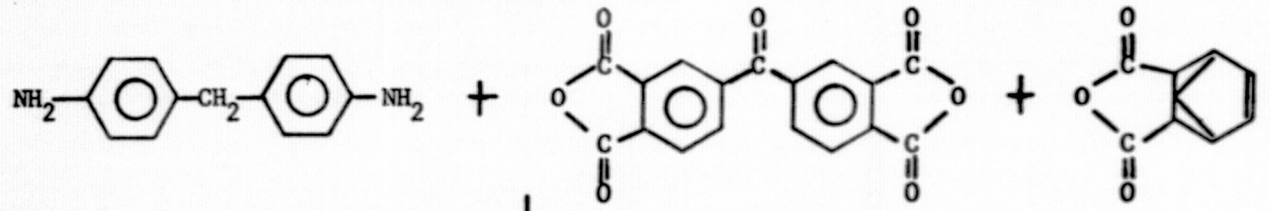
Monsanto 710

Du Pont NR-150B2

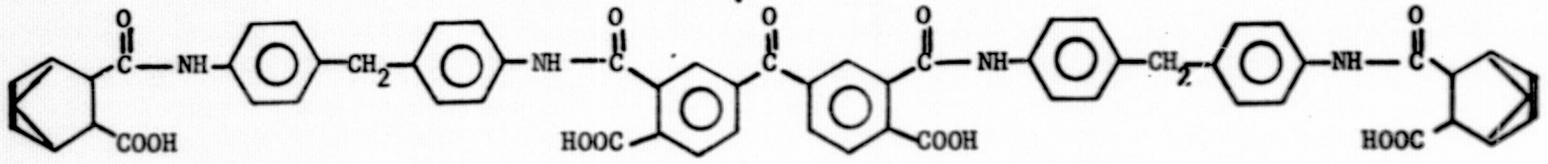
ADDITION TYPE POLYIMIDES

Description	Source	Use	Form
P13N P105A	CIBA-Geigy	Matrix Resin	Solution
Kerimid 601 Kerimid 353	Rhodia, Inc.	Matrix Resin	Solution
F175 F176 F177 F178	Hexcel	Matrix Resin Adhesive	Prepreg Tape
3003	Du Pont	Matrix Resin	Prepreg Tape
PMR 15	--	Matrix Resin	Solution

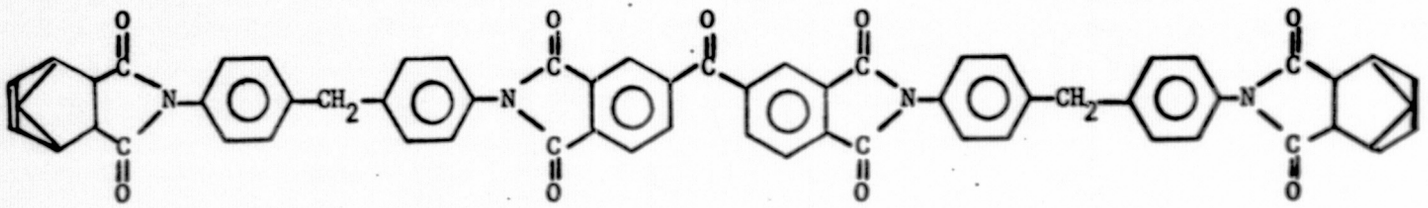
P13 POLYIMIDE CURE *



P13N Amine Acid Varnish



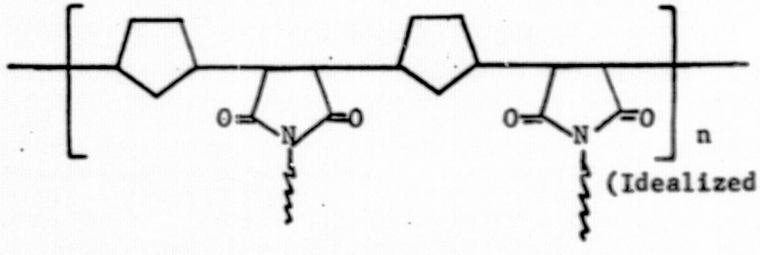
△ 400°F



B-Staged Polyimide Prepreg

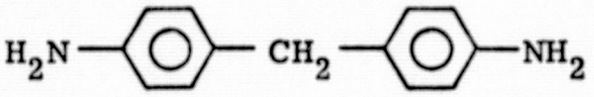
△ 550°F

High MW Polyimide
~2% Volatiles

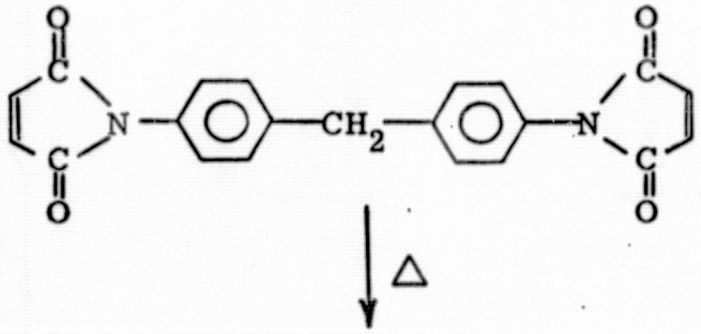


(Idealized Structure)

* Per TRW Systems



Methylene Dianiline



Bismaleimide of
Methylene Dianiline

Chain Extension & Crosslinking via
Vinyl Polymerization & Michaels
Additions. No Volatiles

KERIMID 601 CHEMISTRY

ADDITION PI

PROBLEM AREAS

1) Thermal/oxidative Stability
2) Low Elongation and Toughness
3) Microcracking
4) Occlusion of Solvent
5) Processing Requirements
6) Shelf Life
7) Specifications

THREE GENERAL BLOCKS TO PI TECHNOLOGY

1) Control of Chemistry

2) NDE and QC

3) Large, Complex Parts

CONTROL OF CHEMISTRY

1) Shelf Life

2) Reproducibility

3) Specifications

NDE & QC

A) Resins

B) Adhesive and Composite Prepreg

1) Receiving
2) In House
3) On Tool

C) Finished Parts

1) Adhesive Bonds
2) Finished Parts

LARGE COMPLEX PARTS

1) Adequate Manufacturing Specs

2) Heat Up Rates

3) Control of Processing Variables

4) High T&P for Boardy Material

5) Out Time (Shelf Life) Problems

6) Cleanliness Requirements

REQUIREMENTS, IDEAL SYSTEM

Thermal/Oxidative Stability

Good Toughness, Elongation

No Volatiles

Easy Processing

Close Chemistry Control

Good Environmental Aging

Commercially Available, Moderate Cost

HIGH TEMPERATURE THERMOPLASTICS

Polyarylsulfones

Poly-as-triazines

Thermoplastic Polyimides

Polyphenylquinoxalines (PPQ)

ADVANCES OF HIGH TEMPERATURE THERMOPLASTICS

Demonstrated Thermal-Oxidative Stability

Good Toughness and Elongation

Low Cost Fabrication Potential

Stability and Reproducibility

LOW COST FABRICATION FACTORS

Quick to Continuous Consolidation

Post Forming Capability

Thick Laminates

Ultrasonic Joining

No Chemistry in Production

State-of-the-Art Technology

HIGH TEMPERATURE THERMOPLASTICS

D O N ' T C H A N G E !

In Shipping

In Storage

On The Tool

In Processing

DISADVANTAGES OF HIGH TEMPERATURE THERMOPLASTICS

1) Processing is "Different" for Thermosets

2) Developmental Work is Required

   a) Establish Data Base

   b) Bring Cost Down